MAGYAR TUDOMÁNYOS AKADÉMIA

Műszaki Fizikai Kutató Intézete

MFKI '78

YEARBOOK

of the

Research Institute for Technical Physics
of the Hungarian Academy of Sciences

Институт Технической Физики
Венгерской Академии Наук

Forschungsinstitut für Technische Physik
der Ungarischen Akademie der Wissenschaften

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RESEARCH INSTITUTE FOR TECHNICAL PHYSICS
OF THE HUNGARIAN ACADEMY OF SCIENCES

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Editor:
Tibor SEBESTYÉN

Publisher's reader:
László URAY

Editorial board:
László DOBOS
Márta STAUD
Mrs. Éva NÉMETH

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PREFACE

Dear Reader,

Receiving this book you may really wonder a bit about why this book was compiled, printed and distributed. What was the purpose of investing an appreciable amount of work to summarize the abstracts of papers, some of which you undoubtedly have read in original. The answers are found in the next paper written by our Deputy Director.

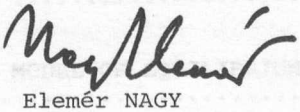
We really want to plan and coordinate research in the firm belief that individual ideas almost always flounder if they are not supported in due time by competent team work.

Time is a prime factor both in fundamental and applied researches, the also rans gain only consolation prizes.

Our planning is centered on the question: are we capable of bringing together a "critical mass" of manpower, equipment and all the other necessary resources which, when successful, yield results important in scientific and/or practical value.

We realize that the larger the critical mass the more ambitious are the aims to be set.

Our Institute with 80 scientists introduces itself with this book to the scientific community, offering partnership and cooperation.



Elemér NAGY
director

PREFACE

CONTENTS

METAL RESEARCH DIVISION

SEMICONDUCTOR RESEARCH DIVISION

STRUCTURE RESEARCH DIVISION

DIVISION OF OPTICS AND ELECTRONIC

20 YEARS OF OUR INSTITUTE

Iván C. SZÉP, Deputy Director

The tasks of post-war reconstruction and rapid industrial development of our country soon have drawn the attention of the Government to the necessity of research. Before World War II. besides the universities only sporadic research activities were performed in industry, with United Incandescent Lamps /TUNGSRAM/ and CHINOIN Pharmaceuticals as the leading companies. These activities were mainly of applied and developmental character. After the nationalization of the industry in 1948 a number of industrial research institutes was founded and the chief scientific body, the Hungarian Academy of Sciences has also organized a network of research institutions, devoted primarily to basic problems of natural and social sciences.

With the advent of technical revolution N°2 the lack of a research center for the new disciplines like electronics, semiconductor physics, materials science became more and more obvious, so the Hungarian Academy of Sciences in 1956 has submitted a draft to establish an independent academic research institute for the investigation of basic problems connected to metal physics, structure of materials and vacuum technology, including the development of new methods of measurement and also of production. Training of young scientists in this particular field was also foreseen among the duties of the new institute.

In 1958 by Government decree the Research Institute for Technical Physics was founded, its prime objectives being basic research in special fields of technical sciences, connected to the needs of lighting /light sources/, telecommunication engineering /electron tubes, semiconductor devices/ and knowledge of material properties. The chief executives of the new institute, G.Szigeti, T.Millner and E.Winter, with long and widely recognized experience recruited a staff of talented gradu-

ates, acquainted them with methods of research,with the technology of materials and devices, with problems existing and gave them a good startup in the fields of interest.

So the outstanding traditions of our lamp industry prompted to carry on research on metallic tungsten, its properties,the role of impurities, which deeply influence its crystalline structure and mechanical behaviour. One should remember that the first practical method to produce tungsten coils for incandescent lamps was patented in Hungary back in 1905. Additives like potassium, silicon and aluminum are known to induce the growth of elongated crystallites which guarantee the non-sagging of the "coiled coils" used in present-day lamps.Millions of millions of electric bulbs are produced all over the world, but we still do not completely understand,how this triad of elements works. During all these twenty years great efforts were made here to find an uncontroversial explanation and it seems to us that today we are very near to it. To come to this point virtually every phase of the preparation has been investigated starting with the chemical and molecular composition of tungsten solutions, the stoichiometry and phase transformations of different oxides of tungsten . Creep, ductility and fracture of tungsten rods, wires were thoroughly investigated and the principal factors governing the process of wire-drawing were determined. Recrystallization of wires was studied with good results and the potassium content of micropores existing on grain boundaries was determined with a highly elaborate electron microprobe technique. It was demonstrated that these micropores play a decisive role in the growth of elongated crystallites, hindering the coalescence of grains in directions perpendicular to their long axis. Besides the technical importance of these discoveries we have got an insight into the basic working principles of metallic systems.

Another group in our institute started work on electron emission, especially of thermionic cathodes used in electron tubes, gas-discharge and fluorescent lamps.New constructions

were developed and new methods of measurement introduced, for which a number of patents was granted, home and abroad.

The persevering problem of burn-out caused by arcing in incandescent lamps was successfully attacked. Means to suppress unwanted ionic emission from coils were found and applied in production.

A large department is engaged in research on luminescent and semiconducting materials. During the first decade new methods for preparation of fluorescent ZnS poly- and mono-crystals were developed, complemented with studies of crystal polytypes and light emission. Later on the interest gradually shifted to semiconductors, where epitaxial growth and hetero-junctions were studied, along with defects of growth. Semi-conductor surface physics became a major discipline, beginning with atomically clean surfaces and atomic arrangement. LEED and field emission technique were applied. Influence of defect and junction planes on transport properties were studied in germanium and gallium arsenide by transmitted phonon drag. Successful experiments were performed to produce silicon-on-sapphire structures and Si-Ge mixed crystals. A wide range of heterojunctions was studied including ZnS - Si, ZnS - CdS and series of $A^{III}B^{V}$ type compounds. Trapping phenomena were investigated based on measurements of thermo-luminescence, thermostimulated current, capacitance-voltage and current-voltage relationship. Extended work was performed on silicon MOS-structures, with particular emphasis on methods of oxide preparation, charge distribution and interface properties.

Optical methods were introduced to determine the concentration of free carriers, luminescence and electro-luminescence spectra were measured and evaluated. Structure and composition of SiO_2 layers grown upon Si wafers were studied with multiple internal reflection. Ellipsometry was introduced to measure optical parameters of very thin insulator layers.

Investigations of material structure were strongly sup-

ported by X-ray technique and electron microscopy. The growing interest in thin films and amorphous layers was reflected in expanded research work upon nucleation processes and phase transformations. The observed influence of substrate orientation upon ordering of deposited layers has raised discussion among specialists.

The second decade of our Institute started under more severe economic conditions. Dictated by the speed-up of economy and more stringent demands on research we had to rearrange our activities, seeking not only basic knowledge but also results which can find immediate application. Since then we have concentrated on refractory metals /tungsten, molybdenum/ and selected problems of steelworking.

Semiconductor research was confined to metal-insulator--semiconductor structures,to new devices, with GaAs, GaP structures and to devices ranking second. Acoustoelectric phenomena and their application were recently introduced. Light-emitting diodes, microwave devices were also fabricated on good level. Up-to-date device technology was strengthened on the whole,and new, powerful equipments for structural investigations were installed.

In this period we have participated in research projects sponsored by ministries and the State Comission for Technical Development. Cooperation with major industrial companies was stressed and new methods for industrial control developed. Work in photometry and color determination of light sources has gained international recognition and has found immediate application in quality assurance.

Technical services have been perfected in the last five years by low temperature facilities established. A wide range of non-commercial testing and measuring equipment was produced to solve some unusual problems, e.g. high-voltage and power generators, programmable controllers, detector circuits, LED photometers. Small-scale manufacturing of these equipments has helped our customers to solve some problems in production and control.

Our international relations have been widespread from the beginning, many of our young coworkers have gained experience and were trained for shorter or longer period abroad in research institutions of USSR, Canada, France, USA, FRG. By their work they have also contributed to the international results of science.

Naturally, all these works have not been hidden behind the doors of the laboratories. Staff members have frequently taken part in international scientific events and reported the results of their work.Near one thousand papers have been published, more than half in international scientific journals and conference proceedings. To exchange views with scientists of other countries, specialised international conferences were organized often here in this country, such as conferences on luminescence /1961, 1966/, on solid state problems /1959/,on electron and vacuum physics /1962/, colloquia on thin films /1965, 1967, 1975/, the pioneering and very successful conference on physics and chemistry of hetero-structures /1970/. It would be impossible to enumerate now the titles of important papers. A comprehensive list of publications have been compiled up to 1975 and is available in printed form.

These days, we are keeping up in many fields with international level and are hopeful about our future prospects. 20 years - this is history for us, which strengthens our self-confidence, that we should always find the right track to pursue and fulfil our tasks laid down in our letter of foundation.

ON OUR FOREIGN RELATIONS

P.Sviszt

International relations enabling the possibility of flowing scientific information among countries play an important role in the development of sciences. Scientific achievements are not only results but they can also serve as the starting points for new research projects. Thus, the development of international scientific cooperations on the basis of mutual advantages is of outstanding importance to all scientific bodies.

Our foreign relations have been growing since the foundation of the Institute and now they are well established and are based mainly on the agreements with scientific institutions of other countries. They contain specific fields of cooperation, common ventures, forming of committees, holding of conferences and also plans for joint works in basic laboratories. These bilateral agreements promote also the mutual visits of scientists, enabling them to get an insight into the work of the partner institute and to perform joint investigations. Such visits sometimes result in common publications.

Important cooperations among the partner institutes of the socialist countries are developed within the framework of the Committee for Multilateral Cooperation of Academies of Sciences of the Socialist Countries in the field of semiconductor research. Main points of this cooperation are the exchange of information on experimental methods and results.

The International Center of Electronmicroscopy in Halle highly promotes the work of our Division of Structural Research. We participate in the Scientific Advisory Board of the Center as well as in the seminars organized by it. Cooperation between our Institute and the Physical Institute at Warsaw and the Semiconductor Institute at Novosibirsk has also begun for invesigating structural disorders.

Common work with the Joffe Institute for Technical Physics

in Leningrad has been carried out in the field of III-V semiconductor compounds. Properties of MOS structures are studied by joint efforts with the Semiconductor Institute of the Ukrainian Academy of Sciences in Kiev.

In the frame of a contract, our Institute promotes the large-scale production of semiconducting light emitting diodes and alpha-numerical displays in a factory of German Democratic Republic. This cooperation between a Hungarian academic research institute and an industrial enterprise in G.D.R. is a good example for cooperations possible.

Our relations with a number of research institutes of different countries are also very active. With the Crystallographic and Mineralogical Institute of Strassbourg University we have begun a joint project for investigating the behaviour of low energy electrons on insulators. An agreement has been signed with the Institute of Technology, Lund, Sweden, for the investigation of the physics of III-V compounds. Another cooperation is established with CISE, Milano for the development and diagnostic investigations of GaAs semiconducting devices. Recently cooperation has started with the Max Planck Institut für Metallforschung, Stuttgart.

Beside the above mentioned scientific cooperations the members of our Institute participate in a number of international organizations as well. They are coordinators in the project on "Properties of semiconducting surfaces, boundary layers and structures" in the frame of the Multilateral Cooperation of Academies of Sciences of the Socialist Countries and are actively engaged in the work of the International Commission on Illumination and of the International Association of Color.

Finally, the extent of our international relations is illustrated by the number of study trips which is often used as an "index" of scientific cooperations. To participate in conferences or to visit institutions our members went abroad in 1978 on 103 ocassions and they spent 1509 days in 16 countries. On the other hand, 185 scientists from 18 countries visited us spending here 843 days. These resulted in 8 joint papers.

SOME GUIDING PRINCIPLES FOR PLANNING RESEARCH

Iván C. SZÉP, Deputy Director

Many senior scientists deny that research can or should be planned. Freedom of choosing subject and objectives of research, in their opinion, belongs to the fundamental rights of the research-minded individual.

Young enthusiasts, on the other side, frequently despise all what was created before they appeared on the scene and are sure that one day they will invent, construct, discover etc. a "big something", if money, assistance, time and credit are given unlimitedly.

Needless to say that both views are extremistic. The majority of scientific workers is well-aware that present-day research is no more what it used to be in 1900 or 1945. Revolutionary discoveries are scarce as before despite the tremendous increase in number of scientific personnel and funds absorbed. Research has become an economic and social activity very similar to industrial production in that it needs funding, investments, qualified manpower, special buildings and technical services. Funds may come from state budget, from authorities responsible for science and development and from industrial customers who set specific tasks to solve. It seems now natural that all these functions and activities need management and organization including planning and concern for utilization of results.

How all these appear in the functioning of our Institute? In the planning system of our country main R+D tasks are subdivided between long-range research plans, under the guidance of the Academy, and industrial development projects administered by responsible ministries. Research trends for the running five-year plan were selected by an advisory board, in accordance with prime industrial objectives. Our Institute has joined in solid-state research with subjects in metal physics and technology, and semiconductor device physics. It was

decided on to participate also in industrial developmental schemes in the field of electronic components especially opto-electronic, microwave, surface-acoustic wave and thin film devices. Research contracts were signed with interested companies, having relation to the general scope of our research conceptions.

Basic principles for selection of research topics were laid down, as:

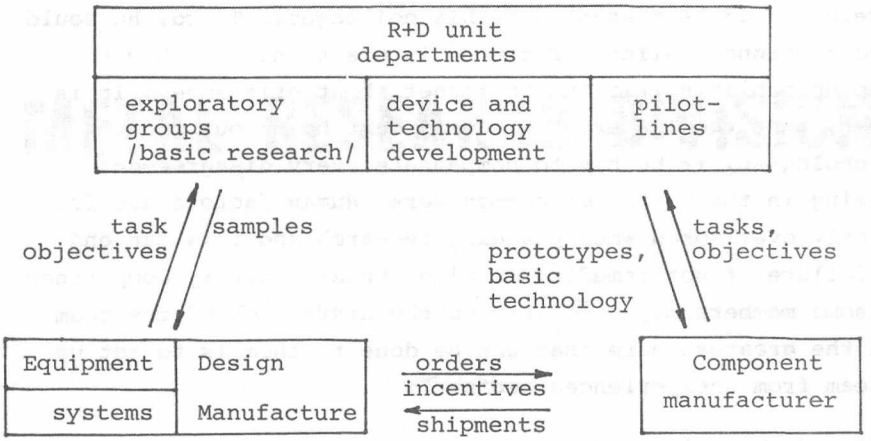
- importance from the view-point of national economy;
- extent of skill and equipment required and at disposal;
- estimated duration of the task and the amount of funds available;
- type of work: basic, applied, experimental or engineering;
- chances for rapid realization of results: in industrial technology, in control and evaluation, as important contribution to science, as patented invention, as a new product etc.

One could object that with these guiding principles serious limitations are imposed upon the course of research, freedom of thought is sacrificed and narrow-minded practicalism may prevail over uncommitted search after new ideas. In practice, nothing of this kind should be experienced. Ruling ideas of science have always come from observations of natural events or man-made experiments. Shrewd theories came always afterwards.

Contemporary science has developed into a motive force of technical progress and to exploit its achievements effectively and to promote its advance, in research establishments a coordinated management system and a well-considered scheme of organization are needed, with enough flexibility to respond to the ever-changing demands and to new scientific developments appearing on the international scene. However, there are very strong links between the current level of

industrialization and the permissible lead-angle of research in a particular country. Big leaps do not pay off even in science, so one has to find the right balance of what can and should be done and when. Sure it is unreasonable to dwell on subjects which can be obtained through international cooperation or trade agreements, but it has to be borne in mind that the most recent inventions or know-how are seldom offered.

The conflict between basic and applied research, study and explanation of phenomena in one respect and the task to develop and define a technology on the other hand, is not a real one and can be easily resolved. The following diagram formulates the main relations in electronic industry between an up-to-date R+D unit, the component and the equipment manufacturer, respectively. The R+D unit is a complex enterprise consisting of departments for exploratory research, where new materials, new phenomena, both experimentally and theoretically are investigated, then departments, where, based on findings of exploratory research, development of new devices and technology is taking place, and in the end, pilot-lines, where the suitability of the technology is tested and the necessary corrections are done. Certainly, the proposal for new devices may come from the component manufacturer too, who at the same time, could have been approached by the design people of the equipment manufacturer. New device technology transferred in proper time to component manufacturer may help him to thrive, and equipment manufacturers when applying new components in their equipment, contribute to the overall progress of the industry. Naturally, they can also formulate the demand for special or even non-existing equipment, where a particular component may play a decisive role. So, for a truly productive research activity a closed double loop must exist between research and production, passing samples, technology, suggestions for application, tasks, supply in one direction and feeding back information on results, demands, formulating tasks, in the other one.



This scheme, of course, may be simpler in other cases where bilateral relations with a single customer are fully sufficient, but a live loop of informations is essential for both parties, too.

When planning research in a scientific institute engaged in technical field, after the selection of appropriate programs and signing the contracts, steps are to be taken to reflect and also to discharge the responsibilities for the respective tasks. Interdisciplinary teams have to be organized according to need, headed by experienced senior scientists, the individual tasks of the participants are formulated, and a system of recording is set up. Quarterly reports are compiled to evaluate progress or backlog in work. Expenditures are controlled by accountants office. Naturally, all this is already routine and nobody would take it as characteristic of planning.

However, interdisciplinary teams frequently are a must for the solution of technical problems. They have to comply with a number of requirements if they are to succeed. First of all, every member should be well trained in his particular field, at the same time unbiased against other fields. Second, he should be able to explain his ideas in a language perceptible to others not familiar with his field, and also to

understand ideas presented by his colleagues. Third, he sould have a strong feeling for common interest and know how to keep up public spirit and to forget about grievances. It is clear, that the leader of the team must be an outstanding psychologist, if he has to compensate every disagreement arising in the course of common work. Human factors are frequently overlooked when planning research and this can end in failure if not remedied in time. Unsatisfactory competence of some members may also lead to the disruption of the team and the greatest harm that can be done to them is to set up a team from unexperienced beginners.

METAL RESEARCH DIVISION

OUR METAL RESEARCH IN 1978

L.Bartha

Tungsten has been studied for several years in our divison and the research aimed to clarify various problems of the K, Al, Si doped non-sag W wire used as filaments in the incandescent lamps.

Intensive theoretical and experimental work has been carried out in order to clarify the mechanism of doping, the formation and chemical characteristics of the non-stoichiometric tungsten oxides and their reduction to metal powder.

In the field of powder metallurgy our research is devoted to the description of the abrupt changes in the various macroscopic properties which are brought about by densification. The aim of our theoretical studies is to clarify the underlying processes of these abrupt changes in the electrical and thermal conductivity, mechanical strength and gas permeability in the framework of the percolation theory.

It is one of the most peculiar features of the mechanical technology of tungsten that swaging and drawing are performed in a temperature region between true warm and cold working. Therefore, the grain boundaries play an unusually important role both in the yield strength and in the electrical transport properties of severely drawn tungsten. This gives rise to a vivid research activity in the field of the grain boundary properties.

Polycrystalline tungsten samples fracture usually along the grain boundaries and the fracture is enormously sensitive

to the presence of carbon and oxygen. Therefore, beside the fracture morphology also the carbon and oxygen uptake from the annealing atmosphere has to be studied. Since the dangerous amount of oxygen is below 10 wt ppm, a new method for the detection of the oxygen uptake was developed.

It is one of the most characteristic features of both the creep and the sintering that the inclusions can change their place by a vacancy-governed bulk motion without dissolution and precipitation. By consequent studies of the accommodation of the inclusion volume to the internal pressure and to the stress state of the matrix and of the coalescence of the inclusions, many features of the creep of non-sag tungsten and the swelling at the practical end of the sintering were clarified.

In recent years similar studies have been carried out on molybdenum metal, too.

Steel research is concentrated on more particular but not less interesting problems than those of the tungsten research.

New methods have been developed for studying:

- detection and control of stress differences and shape defects of cold-rolled steel sheets by magnetic and optical methods;
- desoxidation processes in molten steel measuring the dissolved oxygen concentration by electrochemical method;
- sources and formation mechanism of inclusions;
- special temperature measurements for production control.

For studying the problems mentioned above a great variety of experimental technics is used, like chemical analysis, radioactive tracer methods, thermal analysis, SEM, X-ray methods, electrical resistivity and thermopower measurements, tensile testing etc. Beside fundamental material research there is also technological research in our division. This means that the problems emerging from industrial processes are to be solved with the highest priority and on a broad scientific basis.

CANCELLATION MECHANISM IN THE MAYER-MONTROLL GRAPH SERIES

Z. Demendy

In the equilibrium statistical mechanical theory of liquids the density expansion of the distribution function can be represented as a graph series consisting of so-called Mayer-Montroll graphs.

It is a basic difficulty in this field that there is no rule for the summation of the subseries, in other words the actual degree of an approximation is not necessarily improved by adding more graphs to the theory.

In a recent paper[1] by investigating the physical meaning of various subseries in the pair correlation function g_2 and the triplet correlation function g_3 it has been shown that the graph series of $\ln g_2$ can be rearranged into the sum of three subseries having clear physical meaning.The investigation of the subseries of $\ln g_3$ resolves the old paradox: Why is the superposition approximation good for g_3 and why is this approximation so poor for g_2?

It was also shown that the strong cancellation in the Mayer-Montroll graph series is its inherent property and a physical rearrangement of a graph series is possible only by introducing a new kind of graph bond.

Investigating the asymptotics of the graph series it has been found that the cancellation gradually weakens as the separation of the particles grows.

1. Z. Demendy: "Cancellation mechanism in the Mayer-Montroll graph series"/Submitted for publication in Physica A/

ATOMIC MOTIONS IN LIQUID METALS

T. Geszti J. Kertész

Two problems have been studied: the origin of the oscillatory long-time tail of the velocity autocorrelation function /VAF/[1,2] and an effective field description of the transverse current correlation function[3].

The VAF oscillations can be traced back to the propagation of short-wavelength density waves. In liquid metals the frequency vs. wave number relation $\omega(k)$ for such waves is well defined up to and over a maximum of height ω_m. For both liquid rubidium and sodium this ω_m is equal to the frequency of the VAF oscillations[1]. A detailed hydrodynamic model, the so-called "modified Alder-Wainwright model"[2] - in which for $t = 0$ a particle is represented by a moving spherical region of a continuous fluid otherwise at rest, and for later times $t > 0$ the velocity of the particle is approximated by the flow velocity at the center of the initial moving sphere - has been worked out for this phenomenon. The flow of the fluid is described by /linearized/ generalized hydrodynamics, deviating from ordinary hydrodynamics at high frequencies and for large wave numbers. The results agree well with the computer-simulated VAF not only for the long-time asymptotics but also for intermediate and moderately short times. Moreover, the VAF appears as a sum of a longitudinal and a transverse part, the oscillations being attached to the longitudinal part /i.e. to density waves/, in accordance with Ref.1.

For the transverse current correlation function it is highly non-trivial that a mean-field-like description can exist at all, since the simple physical picture of an averaged potential due to density fluctuations does not work in the transverse case. Nevertheless, a careful analysis within kinetic theory allows one to introduce an ω - and k-dependent quantity of

appropriate symmetry, playing the role of an effective field for transverse current fluctuations[3]. Suitably parametrizing this effective field and fitting the parameters to sum rules, one arrives at numerical results for the transverse current correlation function. Good agreement with computer simulations for liquid Ar witnesses of the reality of the scheme; for liquid Rb there are no simulations to compare with.

1. T. Geszti: "Waves and oscillations in the atomic dynamics of liquid metals" J. Phys. C 9, L263 /1976/

2. T. Geszti and J. Kertész: "Modified Alder-Wainwright model for the velocity autocorrelation function" in "Liquid metals 1976" Inst. Phys. Conf. Ser. No.30, p. 593 /1977/

3. J. Kertész: "Effective-field approach to transverse correlations in simple liquids" J. Phys. C, 12, 1985 /1979/

DIRECT ANALYSIS OF THE CHEMICAL MODEL OF EQUILIBRIUM SYSTEMS

K. Vadasdi

Two basic approaches are known in the literature for the determination of the chemical model, i.e. for the determination of the number and composition of species formed, in equilibrium systems, from experimental / potentiometric and optical/ data:

a/ Partition of experimental data /if possible/ in a way that only a single species dominates in the particular set of data to be analysed. In this case the composition of species can be determined with simple graphical or numerical methods.

b/ "Trial and error" methods based on the computation of stability constants.

In complicated systems where many species are involved with overlapping formation ranges the application of these methods is difficult. Therefore, the applicability of direct computation methods was studied.

In case of potentiometric data the computation problem of stoichiometric coefficients of the species formed was formulated as a nonlinear programming task or as an eigenvalue problem. In case of optical data it was formulated as an eigenvalue problem or as a linear programming task[1,2]. For the calculation of auxiliary quantities /equilibrium concentrations/ a method has been developed based on the Taylor-expansion of mass balance equations[3].

Test computations with synthetic data and those of well known systems show that these methods simplify the problem of

search of equilibrium models. Application for systems of industrial importance is being in progress[4].

1. K. Vadasdi: "On determining the composition of species present in a system from potentiometric data" J.Phys.Chem. 78, 816-20 /1974/

2. K. Vadasdi: "Determination of the complex equilibrium model from potentiometric and optical data" Dissertation, 1977.

3. K. Vadasdi: "Computation of equilibrium concentration without the knowledge of the equilibrium model" Euroanalysis III. Dublin /1978/ p. 160

4. E. Benes, K. Vadasdi: "Direct and "trial and error" analysis of the hydrolitic reaction of polytungstates" /to be published/

ANALYSIS OF DOPANTS AND TRACE IMPURITIES IN TUNGSTEN METAL AND SOME TUNGSTEN COMPOUNDS

P. Tekula-Buxbaum

During the past years some methods have been developed for controlling the industrial manufacturing of tungsten and especially for determination of the traditional additives and impurities. Application of direct atomic-absorption methods has made possible to accomplish a relatively rapid measurement of Na, K, Al, Si, Fe, Mo, Ca and Mg contents of sintered tungsten rods, powders and doped blue oxides[1] / > 1-5 ppm/.

An indirect atomic-absorption method based on extraction of heteropoly-12-molybdic-acids has been developed for measuring As and P contents of ammonium paratungstate powders />10 ppm/. Our first results obtained by this method indicate that there is a considerable />1-10 ppm/ fluctuation in P and As contents of the industrial samples and we have detected rather high levels of impurities even in samples previously considered to be of high purity.

A method has been developed also for measuring sulphur contents by means of an ion-selective electrode. Using this method we have found that the sulphur content has a stepwise increase from an initial value of 1 ppm in ammonium paratungstate to a value of 20-60 ppm in tungsten wires.

1. P. Tekula-Buxbaum: "Determination of Small Quantities of Aluminium and Silicon in Tungsten metal and Tungsten Oxides by Atomic-Absorption Spectrophotometry" Microchim. Acta I/1-2, 145-150 /1977/

PREPARATION AND THERMAL DECOMPOSITION OF AMMONIUM METATUNGSTATES

E. Benes
M. Farkas-Jahnke[+]
T. Grósz[+]
K. Vadasdi

The different ammonium-paratungstate /APT/ species used for the production of metallic tungsten are well known, thoroughly studied compounds. Much less efforts have been devoted to the study of ammonium-metatungstates /AMT/. Though the isomorphism between metatungstates and heteropolytungstates was already presumed at the beginning of this century, the structure of AMT-s has not been determined till now mainly because of their instability.

AMT species have been prepared by different methods for the determination of their basic structural character, the study of their thermal decomposition and the identification of the products formed.

The three methods for preparation /ion exchange, dissolving tungstic acid in APT solution, acidifying APT solution with strong mineral acid/ yielded materials of somewhat different structure. According to their X-ray patterns taken in a Guinier-de-Wolff-type focusing camera with CuK_{α} radiation, they are mixtures of differently hydrated AMT species. Even in air and at room temperature the line system of the materials changed after some weeks indicating a slow transformation in the hydrated state of the samples.

By slow crystallization of AMT-s transparent, clear crystallites were obtained. As determined from the distances of layer lines on oscillation patterns taking the axes indicated on Fig.1. as oscillation axes, periodicities of 1.24, 1.24, 1.72 nm were respectively determined in the three directions. The crystallites preserve their perfect structure only in contact with their mother solution. When dried, a

[+]Department for Structure Research

rapid recrystallization resulting in an aggregate of white grains takes place.

The effect of a heat treatment at 300°C was similar on all types of AMT-s. At first, the diffraction lines became more and more diffuse and were shifted corresponding to decreasing lattice spacings. After 6-8 minutes of heat treatment one strong diffuse line around 0.85 nm remained, suggesting that after thermal decomposition larger complexes of diameter 0.85 nm still exist. While a major part of ammonium and water can be supposed to have left the material till that time, the assumption is that this complex is formed of WO_6 octahedra similarly to the "Keggin-complex"[1] /Fig.2./. The elementary cell of the different AMT-s can be built up from this complex ion, connected by water and ammonium bridges similarly to that in phosphotungstates. After further heat treatment diffuse lines indicating the bonding of the complexes into a lattice with hexagonal symmetry appear and increase in intensity,while the intensity of the 0.85 nm line is decreasing. The patterns of one of the samples contain also the diffraction line system of a cubic ammonium tungstate with pyrochlore-like structure. Lattice parameter $a = 1.008_7$ nm is derived from the measured position of the lines; the observed reflections indicate a space group $Fd3m\text{-}O_h^7$. The composition of this compound can be formulated as $/NH_4/_2O \cdot 4WO_3 \cdot H_2O$.

1. R. Allmann, H.d'Amour: Z.Krist. 141, 161 /1975/

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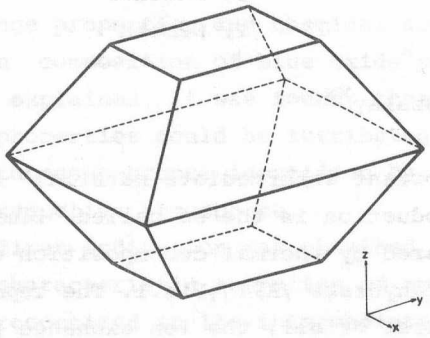

Fig.1. Typical crystal shape of AMT

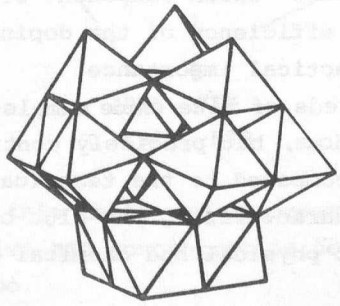

Fig.2. The "Keggin-complex" built up from WO_6 octahedra

THE STUDY OF THERMAL DECOMPOSITION PRODUCTS OF AMMONIUM PARATUNGSTATE

L. Bartha
B.A. Kiss[x]
T. Millner
T. Németh
T.Szalay[xx]

One of the most important intermediate material of the NS /non-sag/ tungsten production is the so called "blue oxide". This solid phase is prepared by thermal decomposition of ammonium paratungstate pentahydrate /APT/,Fig.1. The reproducibility of properties - first of all, the ion exchange properties - of the non-stoichiometric, multi-component blue oxide seems to be the main requirement of homogeneity in tungsten technology.

As it was shown in our earlier papers[1-4], the incorporation of doping elements, needed for creep-resistent, high quality incandescent lamp filaments can be achieved through ion exchange, ion association and electron exchange properties of blue oxide.

As it is well known,a good doping needs steady-state conditions for the interaction of doping elements and tungsten oxides. Therefore, one has to know which component of the blue oxide is responsible for the efficiency of the doping. The right answer seems to be of practical importance.

More than two hundreds of blue oxide samples have been prepared in our laboratory at various, but precisely controlled environments. They were studied and compared to the technical blue oxid samples. The properties characterizing the blue oxides were investigated using different physical and chemical methods. The

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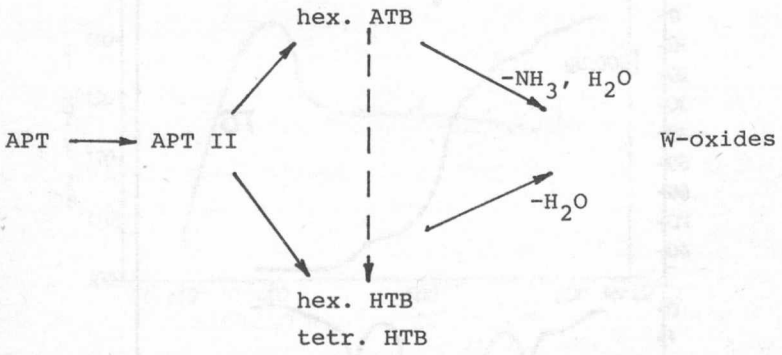
[x]Research Institute, United Incandescent Lamp and Electric Co. Budapest, Hungary.

[xx]Institute of Physical Chemistry of Kossuth Lajos University, Debrecen.

complex evaluation of results based on data obtained by X-ray, mass spectrometric, infrared absorption, potentiometric, radioactive tracer, neutron activation, vacuum annealing and thermoanalytical methods. Taking into account these data, the varying ion exchange properties and chemical activities /Fig.2./ depending on composition of blue oxide samples could be successfully explained. It was found, that the changes of doping activity properties could be attributed to the component hydrogen-tungsten-bronze identified by us in the samples prepared in reductive atmosphere.

The first indication was obtained in our earlier studies[5] when the characteristic anomalies of ammonium paratungstate were recognized in its intermediate decomposition products at low temperatures. This was the change of the acidic character of APT II as a function of decomposition temperature.

In conformity with the results, the decemposition mechanism of APT can be described as follows:



According to this multi-way decomposition model, the change of the active HTB concentration could be described mathematically, too.

The mechanism suggested above has given some hope to optimalize and control the tungsten technology in a new way.

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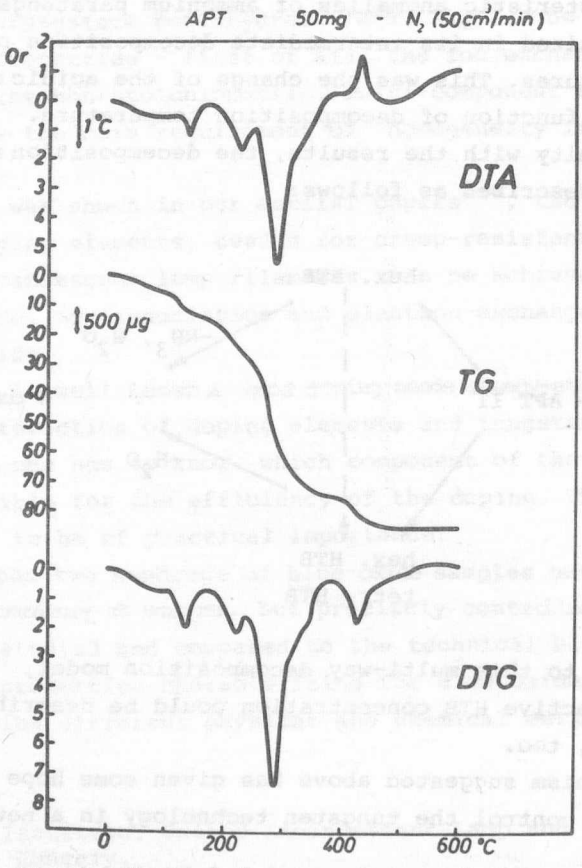

Fig.1. Thermal decomposition of APT

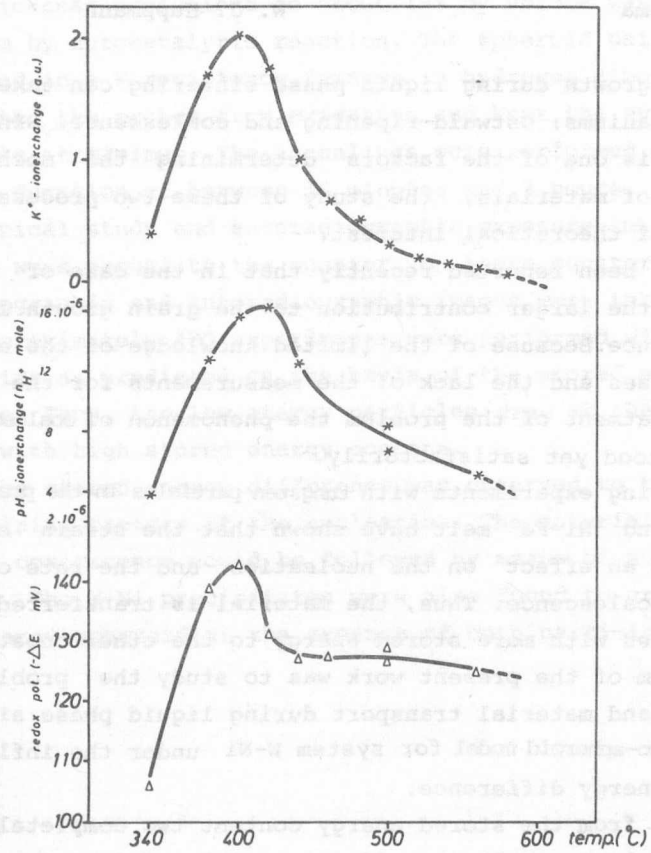

Fig.2. Ion exchange property and chemical activity of blue tungsten oxides depending on decomposition temperature.

STUDY OF THE PROCESSES OF LIQUID PHASE SINTERING BY MEANS OF AUTORADIOGRAPHY

L. Kozma W. J. Huppmann+

Grain growth during liquid phase sintering can take place by two mechanisms: Ostwald-ripening and coalescence. Since the grain size is one of the factors determining the mechanical properties of materials, the study of these two processes is more than of theoretical interest.

It has been reported recently that in the case of W-based composites the larger contribution to the grain growth is due to coalescence.Because of the limited knowledge of the elementary processes and the lack of the measurements for the qualitative treatment of the problem the phenomenon of coalescence is not understood yet satisfactorily.

Sintering experiments with tungsten particles in the presence of liquid Ni and Ni-Fe melt have shown that the strain energy content has an effect on the nucleation and the rate of the growth by coalescence. Thus, the material is transferred from the particles with more stored energy to the other ones.

The aim of the present work was to study the problem of nucleation and material transport during liquid phase sintering of the two-spheroid model for system W-Ni under the influence of stored energy difference.

Apart from the stored energy content two completely identical W single crystal spheroids were sintered in pairs in the presence of liquid Ni. The spheroids were produced by plasma spraying. To ensure the required difference of the stored energy within the spheroid couples a batch of particles were submitted to recrystallization. On the basis of previous works the non-recrystallized particles were presumed to take part in the

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+Max-Planck-Institute for Metals Research, Institute for Materials Sciences, Stuttgart, Germany

material transport of the coalescence while the others remain unchanged. Therefore, the high energy spheroids were labelled with W-187 isotopes obtained by nuclear reactor. A Ni layer of the thickness equivalent to about 15% by volume was deposited on them by autocatalytic reaction. The spheroid pairs were then sintered in a W resistance furnace in hydrogen atmosphere, which protected the probes from oxidation and kept the evaporation of the melt at minimum. The annealings were performed at 1500°C with a duration of between 15 minutes and 3 hours. For the microscopical study and autoradiographic exposure the coalesced probes were ground to the equator. On these equatorial planes metallographic and autoradiographic images were taken.

Approximately 400 experiments were performed with the spheroids as predicted on the basis of the stored energy difference. Thus, the low energy particles grew at the expense of those with high stored energy content.

The stored energy difference was observed to be one of the determining factors of the nucleation. The material transfer during coalescence could be followed by means of autoradiography. The W-Ni precipitates were also found to grow on the low energy spheroid at the expense of both particles.

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DEVELOPMENT OF INSTRUMENTS FOR DIFFERENTIAL THERMAL ANALYSIS

L.Bartha K.Németh
Cs.Lénárt T.Németh
E.Nagy

The physical and chemical transformation of materials is nearly always accompanied by measurable enthalphy change.This takes place at characteristic temperatures so its measurement helps in identifying the materials or in clarifying the mechanism of the process involved.

In thermal analysis the temperature of a sample is measured as a function of time and a heating or cooling curve is recorded. In this technique /DTA/ the sample temperature is continuously compared to a reference material temperature,the difference in temperature beeing recorded as a function of temperature or time.

In our instruments /the first is patented only in Hungary but the second in several countries/ both sample holders have their own heating elements, their own control temperature sensors and their own sample temperature sensors attached to the thin wall of the sample holders. The sample temperature sensors are connected to a recorder and/or a data processing system.

The arrangement of the sample holder makes possible the measurement of the power difference,too /Fig.1 /.

Based on the above described layout, one can analyse very small samples with a large accuracy. Due to the precisely controlled thermal conditions outstanding thermal sensibility, reproducibility and resolution can be obtained.Due to the arrangement of the heating-element the equipment is characterized by a fast heating rate in a wide temperature range, and the measurements can follow each other without any time delay. The instruments can be used in a temperature range of -150^{o}C to +750^{o}C. The DTA-TG instrument is a compact desktop thermo-

gravimetric and differential thermal analyzer designed for simultaneous measurement of both DTA and TG /weight changes/ of samples.

The development of a complete thermoanalytical family of instruments is foreseen, which contains a DTA equipment operating on high temperature and TG instrument of great precision.

Our instruments have been successfully applied in studies of phase transformations /e.g. melting and supercooling of pure metals, alloys and compounds, structural changes etc./, of solid state and gas-solid reaction kinetics /e.g. precipitations, diffusion compositions/, of chemical stabilities /e.g. drugs, ores, inorganic compounds/.

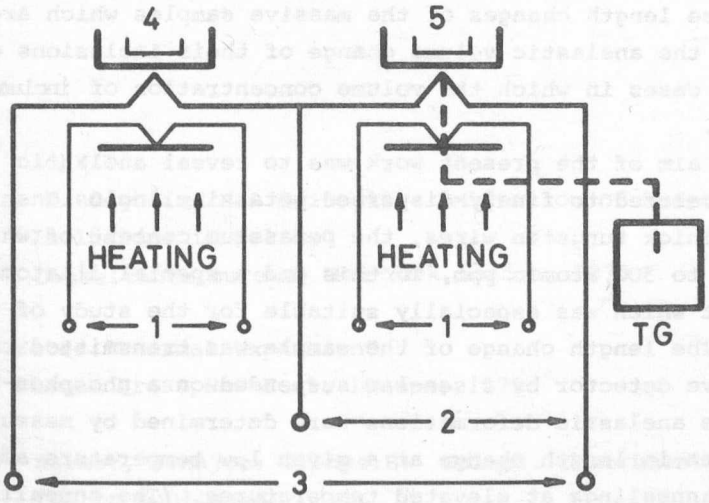

Fig.1. Scheme of DTA /-TG/ instruments
/1-control thermoelements, 2-temperature signal, 3-DTA signal, 4-sample, 5-etalon/

ANELASTIC VOLUME CHANGE OF POTASSIUM INCLUSIONS IN TUNGSTEN

P. Harmat J. Major

I. Gaal

Many high temperature processes which originate from crystal imperfections bring about diffusion controlled changes in the volume and/or in the shape of bodies. To this class of phenomena belongs also a great variety of anelastic processes in which the accomodation of the inclusions to various external parameters like temperature and tensile stress is diffusion-controlled[1]. The anelastic volume change of inclusions escapes direct observation /e.g. by transmission electron microscopy/ because the anelastic changes are small. Owing to the high resolution of dilatometers[2], it may be possible, however, to detect those length changes of the massive samples which are related to the anelastic volume change of their inclusions even in those cases in which the volume concentration of inclusions is small.

The aim of the present work was to reveal anelastic length changes related to finely dispersed potassium inclusions in 180 /um thick tungsten wires, the potassium content of which amounted to 300 atomic ppm. To this end a special dilatometer was built which was especially suitable for the study of thin wires[3]. The length change of the sample was transmitted to a capacitive detector by a see-saw suspended on a phosphor-bronze leaf. The anelastic deformations were determined by measuring the frozen-in length change at a given low temperature after various annealings at elevated temperatures. /The annealings were performed within the dilatometer by self-resistance heating./ It turned out that the relative accuracy of the length determination /in our case $2 \cdot 10^{-7}$ for a sample lenght of 20 cm/ was limited by the stability of the temperature distribution in the sample and in the dilatometer frame.

By changing the tensile stress cyclically at 2200 K and at an oxygen partial pressure of 10^{-3} Pa, the length of the sample changes cyclically, too. /When, for example, the sample had been equilibrated at a higher tensile stress, then after an annealing under a lower tensile stress the sample shrank./ The relexation time of the anelastic length change was governed by self--diffusion, as expected[1]. /Let us realize that if, for example, the internal pressure is larger than the surface pressure, then vacancies are emitted from the interface, and their absorption on various dislocation sinks leads to the observed shrinkage./

The magnitude and kinetics of the anelastic length change were in good agreement with the theoretical predictions, if it was taken into account that the inclusions were filled with a very dense potassium gas, the pressure of which was larger than the critical one[4].

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CAVITY FORMATION DURING HIGH TEMPERATURE CREEP IN BUBBLE STRENGTHENED MATERIALS

O. Horacsek K. Horacsek

The effect of gas bubbles in solids was investigated on the high temperature creep properties of tungsten filaments produced by powder metallurgy. It was found, that the potassium-filled submicroscopic bubbles formed in KSiAl-doped tungsten play a significant role in the creep rupture of the wire. Under a uniaxial stress of σ = 13 MPa at T = 2800 K the lifetime and creep-ductility of this material are controlled by the rate of growth of the bubbles. In the pure /undoped/ tungsten wires, however, the dominant mode of cavity formation leading to fracture is the growth of microcracks generated continuously during deformation.

The investigations have shown that the possibility of the coalescence of moving bubbles in KSiAl-doped tungsten filaments during high temperature creep can lead to cavity formation even at stress levels which are considerably lower than the theoretically predicted critical stress. In this case the cavity formation is a result of several subsequent processes. In the first period of the void growth some gas accumulation is required for the bubble to reach a critical size. The subsequent growth of this nucleus is due to the condensation of lattice vacancies and the pressure within the cavity decreases steadily. Theoretical considerations predict, however, that the decrease of the internal pressure is limited.

At a later stage of growth process, when the cavity radius is much greater than the spacing of the bubbles, the pressure inside the cavity is given by

$$p = \frac{\varrho \cdot c \cdot RT}{A}$$

where ϱ, c, A, R and T are the density of the metal, the concentration and the atomic weight of the bubble-forming material, the gas constant and the absolute temperature, respectively.

It is remarkable that at this time p is already independent from the cavity size, i.e. during isothermal annealing of the sample the internal pressure is determined solely by the concentration of bubble forming material. The development of the constant pressure inside the void is due to the impossibility of diffusion of gas atoms which are insoluble in the matrix.

During cavity growth the surface tension associated with the void decreases monotonically. If the surface tension is already less than the "volume-independent" internal pressure given by the equation, the growth of the cavity is possible in principle even at zero external stress. Consequently, at a later stage of cavitation in bubble strengthened materials additional internal forces promote the void growth contributing to the failure.

Metallographic examination have revealed, that void may be formed in the tungsten filaments during the life of incandescent lamps due to the motion and growth of the bubbles. This suggests, that in addition to the well known non uniform evaporation mechanism related to surface defects on the filament, diffusion processes within the wire could also play a significant role in the deterioration of the coil.

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INVESTIGATION OF THE THERMALLY ACTIVATED PLASTIC DEFORMATION

A.T. Nagy

The thermally activated plastic deformation of some cold worked bcc metals was investigated at room temperature using stress relaxation technique. On as-received tungsten and molybdenum wires as well as on thin steel sheets the activation volume of dislocation motion was determined by Conrad analysis. Using the Li analysis carried out by graphical method the flow stress was divided into effective and internal stress, and the velocity-stress exponent was determined. According to our results the same dislocation mechanisms can be assumed to work in the cold worked materials as in the single crystals or well annealed polycrystals of the metals in question. This statement is based on the experimental results, namely, on the activation parameters measured by us which are not very different from the values measured on samples without cold working, taken from the literature.

The effect of internal stresses, ranging over several crystallites, on the measured parameters was investigated by computer calculations. On the basic of these calculations the correction of the experimental results as well as the detection of these stresses are possible.

The instability of uniaxial tension was investigated by computer calculations, and the ultimate elongation of tungsten wires was explained.

The graphical methods applied till now have proved to be insufficient for further work. Thus, an automatic data processing for evaluation of relaxation curves was worked out.

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ON THE TEMPERATURE DEPENDENCE OF THE EXCESS RESISTIVITY IN DILUTE VOLATILE ALLOYS

L. Uray T. Vicsek

Refractory metals, and especially tungsten, have the peculiar property that their common substitutional solutes are volatile and during various treatments at high temperatures the surface region is depleted in volatile solutes. Therefore, in the thin recrystallized wires of many refractory alloys an appreciable part of the temperature dependence of the excess resistivity is related to the radial distribution of the volatile solutes /extrinsic temperature dependence/. Both the extrinsic and the intrinsic part of the temperature dependence have been determined for dilute WFe, WCo and WRe alloys, by measuring the resistance as a function of the temperature and the thickness of the layers removed by electrothinning, Fig.1. From these data the parameters of the evaporation profiles were also determined. According to Fig.1, the WCo alloy is a Kondo system,[1] since its resistivity shows a minimum at about 20 K .

In the surface region at low temperatures, where the concentration varies rapidly within a mean free path, the local resistivity concept becomes invalid, and the resistance of the sample has to be calculated directly from the Boltzmann equation. This is the so-called microscopic case. /In the macroscopic cases the concentration change is negligible even within distances corresponding to a few mean free paths and thus the local resistivity concept is valid./Further on[1] the temperature dependence of the excess resistivity for experimentally determined evaporation profiles was calculated both in the macroscopic and microscopis cases, by making use of the intrinsic temperature dependence of the excess resistivity shown in Fig.1. In the treatment of the microscopic case we followed up the work of Geszti[2]. Our experimental results agree very well with the results of the microscopic calculations. The macroscopic calculations give erroneous results as expected.

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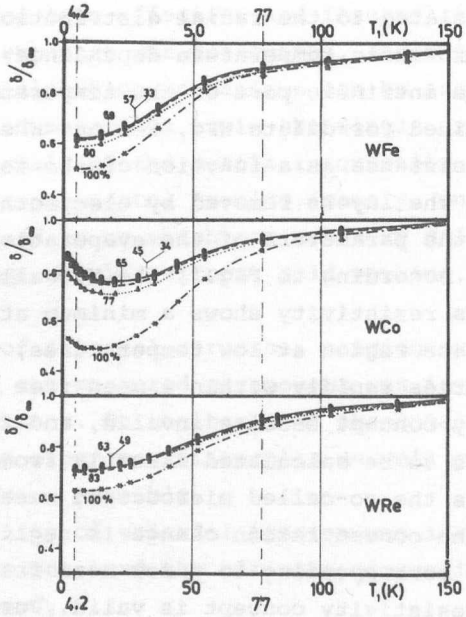

Fig.1. Measured values of the normalized excess resistivity $\delta(T)/\delta(\infty)$ as a function of the temperature for various dilute tungsten alloys. The numbers on the curves give the relative diameters in percent after electrothinning. δ_∞ is the high temperature limit of δ now measured at a temperature $T \approx 200$ K.

GRAIN BOUNDARY ELECTRICAL RESISTIVITY IN TUNGSTEN

A. Barna[+]
I. Gaal
O.Geszti-Herkner[+]
J. Neugebauer[++]
Gy. Radnóczi[+]
L. Uray
T. Vicsek

Since the resistivity contribution of grain boundaries depends also on the angle between the current density vector and the normal vector of the boundary, it is of interest to investigate the grain boundary scattering on structures for which most of the grain boundaries are either parallel or perpendicular to the direction of the current density vector. In heavily drawn and partially annealed K-Al-Si doped tungsten most of the grain boundaries are parallel to the wire axis[1]. Thus, they are parallel to the direction of the current density vector of the usual dc measurements. This material represents, therefore, a useful model for the study of the grain boundary resistivity.

Thus, we have firstly attempted to characterize in details the defect structure of tungsten wires, swaged and drawn to a diameter of 0.18 mm according to the standard commercial practice. Transmission electron micrographs, selected area diffraction patterns and dark field images taken on the transverse section of the wires showed that after various annealings between 1600 K and 2400 K the so called fibre structure was an ordinary grain structure in which the radial orientation of each fibre around the common <110> texture axis was independent of the orientation of the adjacent fibres, and the boundaries revealed by the transmission micrographs are in 80 per cent

[+]Division for Structure Research

[++]University for Heavy Industry, Miskolc

high angle grain boundaries. On the transverse micrographs the cross section of the fibres was nearly equiaxial[2]. Thus, the ribbon-shaped transversal cross sections found by Meieran and Thomas on thicker wires[3] have to be looked on as an effect of swaging. During the coarsening of the fibre structure the frequency of the 120° edges increases extensively on the transverse sections[2].

By assuming that the electrons are scattered in a purely random fashion by the grain boundaries, the free-electron theory yields the following expression for the excess resistivity of an elongated grain structure[4]:

$$\rho(T) - \rho_p(T) = 3/8 \cdot \lambda_p(300\ K) \cdot \rho_p \cdot (300\ K) \cdot S \qquad /1/$$

where $\rho(T)$ is the total resistivity at temperature T, ρ_p denotes the resistivity of pure tungsten, λ_p is the mean free path of the electrons in pure and defect free matrix, and S is the grain boundary area for unit volume / $\lambda_p(300\ K) = 38nm$/. The resistivity given by Eq.1. is measured parallel to the elongated structure at temperatures, where λ_p is much smaller than the grain size. By comparing the measured resistivities and grain boundary areas, it turns out that Eq.1. overestimates the scattering power of the grain boundaries by a factor of two. This finding can be taken into account by a correction factor p = 1/2 which accounts for the fact that the electrons are not scattered in a completely random fashion by the grain boundaries[2].

For grain boundaries parallel to the current density vector, the excess resistivity has a maximum at a temperature , where the mean free path in the grains is nearly equal to the grain diameters[5], and the parameters of the maximum depend on the correction factor p. This maximum was revealed experimentally on the partially annealed wires and p was again about 1/2.

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ON THE TUNGSTEN-OXYGEN SYSTEM

I. Gaal J. Major
A. Kele L. Uray

In order to avoid the difficulties connected with the chemical analysis of oxygen in refractory metals[1], the rate of oxygen uptake was measured via the internal oxidation of aluminium dissolved in tungsten. Since during internal oxidation the solutes precipitate as oxide inclusions, the rate and extent of oxygen uptake can be determined by means of electrical resistivity measurements. If the stoichiometry of the formed inclusions is known, one can easily determine the changes in oxygen concentration between 10 and 100 atomic ppm.

By means of diffusion annealing, tungsten-aluminium alloys were prepared, with an aluminium concentration of between 100 and 200 atomic ppm. /The solute content of the starting material was well below this level./ In the 180 /um thick samples the time needed for the oxidation of 100 atomic ppm aluminium[2] amounted to several hours at 2400 K at an oxygen partial pressure of 10^{-3} Pa. This very sluggish oxygen uptake has to be ascribed to the very low value of the stationary oxygen concentration, since according to Piguzov et al[3] the diffusion constant of oxygen is high in the refractory metals, too. A direct evidence for the low concentration of dissolved oxygen was given by the quenching experiments: after quenching from 2600 K, for example, the resistivity decrease due to an annealing at 1200 K was less than 0.1 per cent of the room temperature resistivity[4], and thus the concentration of the quenched-in solute oxygen was lower than 50 atomic ppm[5]. This low apparent solubility of oxygen in tungsten can be ascribed to the volatility of the tungsten oxides: the oxygen molecules encountering the tungsten surface evaporate, i.e. they form tungsten oxide molecules with a very high probability and condense on the cold walls of the vacuum chamber, so reactions between the tungsten oxide gas and

the solid tungsten cannot take place.

In accordance with the thermodynamical expectation, aluminium oxide is reduced to aluminium dissolved in the tungsten matrix at 3000 K in a vacuum[2] with an oxygen partial pressure lower than 10^{-4} Pa. In dry hydrogen the reduction takes place also at lower temperatures .Therefore, during the usual sintering of doped tungsten the aluminium oxide inclusions should be reduced to aluminium dissolved in tungsten[2].

On the other hand, it is well known that aluminium oxide inclusions can be found also in some swaged rods[6]. This finding might be ascribed to the fact that in some rods a few gas percolation paths are still open, where the concentration of tungsten oxides is nearly the equilibrium one and thereby the concentration of the solute oxygen in the matrix might increase appreciably due to reactions between the oxide gas and the solid.

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ON-LINE MAGNETIC SHAPE METER FOR STEEL STRIPS

P. Ivanov
I. Gaal
E. Hauszner+
J. Major
J. Gráner
D. Zsámbók+

It is well known that the non-developable shape defects in cold rolled strips arise because the strips have not been rolled uniformly across their width. This kind of inhomogeneous plastic deformation brings about elastic stresses in the strip, even if it is placed unrestrained on a flat level surface. Recently, Buchholtz[1] has drawn attention to the fact that even minor variations in plastic elongation across the strip width give rise to internal stresses large enough to cause elastic buckling of which the most common forms are known as center and edge waves. Although the tension level at modern rolling mills is almost always high enough to eliminate the elastic buckling while the strip is on the mill, the inhomogeneous plastic deformation will still give rise to internal stresses. Thus, the distribution of the total stress across the width of the strip will indicate the shape defects of the unconstrained strip.

Our Institute and the Steel Works of Dunaujváros have developed a special kind of magneto-elastic non-contact shape meter[2] which measures the stress distribution across the strip width during high speed rolling. The main point is that the exciting flux is stabilized by electronic means against the vibration of the strip, in order to detect stresses with the same sensitivity at every possible position of the strip. The stress differences across the strip width are displayed on a TV screen. Using this device, mill operators are able to correct the latent shape defects by roll bending. Of course the signals are also available for an automatic mill operation.

+ Steel Works of Dunaujváros

During a mill trial the instruments suffered no damage and performed satisfactorily. If the current theory of strip buckling at its face value is taken, it might be concluded that there was a good agreement between the stress distribution displayed on the screen and the shape defects observed visually on supported horizontal strips. By means of the shape meter it was possible to produce strips showing only fine deviations from the flatness /according to DIN 1541/.

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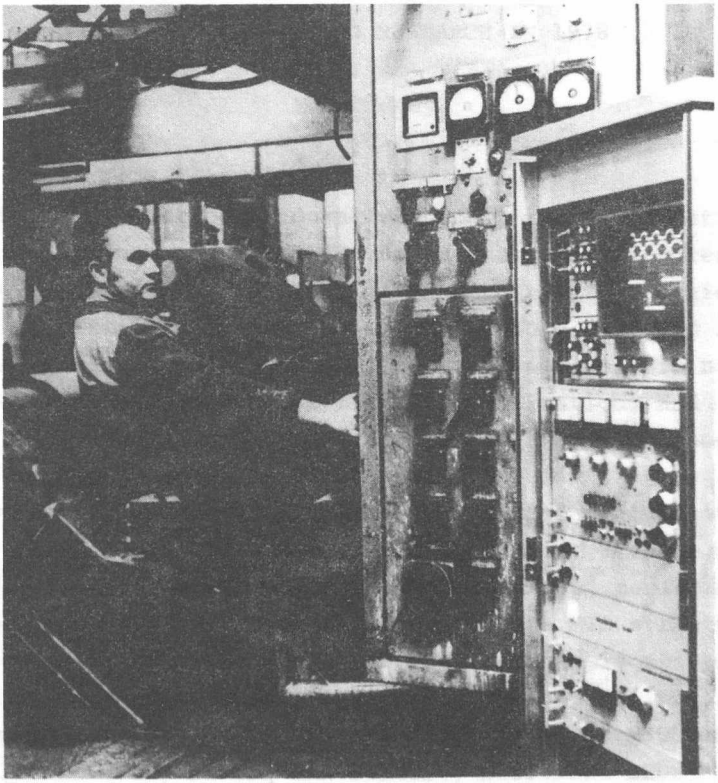
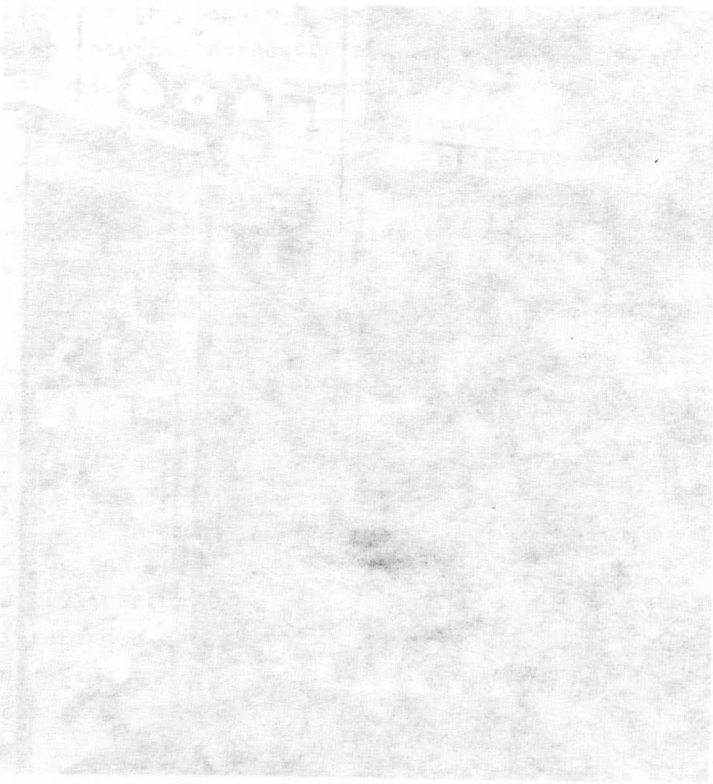


Visual observation of the distribution displayed on the screen of the magnetic shape meter installed in the Steel Works of Dunaujváros for controlling the mill operation



SEMICONDUCTOR RESEARCH DIVISION

OUR SEMICONDUCTOR RESEARCH IN 1978

E. Lendvay

This short introduction allows only the illustration of our activity in the various fields of semiconductor research. In 1978 the Semiconductor Section of our Institute achieved several interesting results which the readers can find in the relevant parts of the Yearbook. These, of course, are not able to cover all details but the original publications and reports listed after each contribution contain every data necessary to the full understanding of our activity.

Our staff consists of 74 members, 35 with university degree. There are three fields of our interest: /i/basic research and device development related to the $A^{III}B^{V}$ semiconductor compounds; /ii/ research on Si based MOS and MIS structures; /iii/ acoustoelectrical phenomena and their applications.Our scientists worked on delicate scientific problems, too, and developed different solid state devices, such as MNOS memory cell, linear CCDs, $LiNbO_3$ SAW filters, different LEDs and microwave Gunn and Schottky diodes as well. Investigations of great interest have already been carried on for years by us in the study of recombination, transport and domain proc - esses, the technology of semiconductors and developing different measuring techniques.

From our $A^{III}B^{V}$ technological research the last year's most prominent results were the construction and building of an automatic vapor phase epitaxial reactor for GaAs, the development and putting into operation of several new LPE systems for multilayer $A^{III}B^{V}$ structures. Using these equipments epitaxial $A^{III}B^{V}$ layers of high quality were grown by VPE and LPE methods for our device development activity.

The wafer and multilayer parameters were measured by He--temperature photoluminescence, SEM, galvanomagnetic, thermostimulated and capacitive methods. The main goal of these efforts was the reproducible production of GaAs epilayers of high purity /$5x10^{14}$ - $5x10^{15}$ cm^{-3}/

Successful preliminary experiments have started to synthetize macrocrystalline, inclusion-free $A^{III}B^{V}$ boules from pure gallium produced by the Hungarian Ajka Aluminium Work to test whether our mostly used materials /quartz, graphite etc/ and methods /SSG, Bridgman/ can be applied to transform the metallic Ga into semiconductor grade $A^{III}B^{V}$ materials. In the year 1978 work started to extend our earlier results to develop GaAlAs-based IR LEDs for medical applications. We established an intensive collaboration with Werk für Fernsehelektronik, Berlin, on LED and display development by using up-to-date methods of deep level spectroscopy in order to study degradation phenomena. Research was continued to complete our microwave program for developing the high power Gunn and Schottky LID structures.

In the silicon field the design and production of polysilicon-gate linear CCDs up to 32 bits were completed in the year. In this context high quality oxide layers were grown by different methods and the parameters of the technology have been optimized. This oxide research was also applied for MNOS EAROM structures using chemically produced thin oxides /1.6 - 1.7 nm/ and Si_3N_4 layers grown by CVD techniques. Interesting results were gained regarding the dependence of the memory properties and the layer structures involving the

chemical structure. The number of the Si-N and Si-H bonds were studied by reflexion IR spectroscopy, and their definite connection with the device properties have been found. During the development of FAMOS memories, our groups together with Research Institute for Electronical Industry /HIKI/ developed measuring techniques for FAMOS characterization.

In close cooperation with the Research Laboratory for Crystal Growth of the Hung. Acad. Sci., work on the processing of $LiNbO_3$ /orientation, cutting and polishing/ was done producing slices for our SAW filter development. The filters, especially those needed for the color TV-s, were also developed with the necessary amplitude and group delay characteristics.

In supporting the technology our groups put into operation a fully automated van der Pauw measurement, Dew-point measuring equipment, different data acquisition and processing systems. In cooperation with the institute MIKI an on-line system designed earlier is being under installation. In the device laboratories the mask design, the metallization techniques and the photolithographic technology were adapted to our needs. Besides, in the same period we organized two international seminars on $A^{III}B^{V}$ LED research and on the measuring techniques of the highly compensated $A^{III}B^{V}$. Three of our coworkers obtained scientific degree /Candidate of Sci./ and two others have finished their thesis.

By summarizing we may conclude that this was a successful year for our groups. We hope that the reader will get a good insight into the problems and the results of the Semiconductor Division.

HIGH PURITY GaAs LAYERS GROWN BY VAPOUR PHASE TRANSPORT

T. Görög I. Gyuró

The development of the different GaAs devices /e.g. Gunn, Schottky and IMPATT diodes/ requires production of good quality GaAs epitaxial layers. According to some authors[1,2] the major back-ground impurity in the VPE GaAs layers is silicon from open flow quartz systems. It is also generally known that the $AsCl_3/H_2$ mol fraction determines the incorporation of the silicon. In our laboratory we have designed and built an epitaxial reactor system using our previous experiences[3]. The process is based on Effer's method[4], where an $AsCl_3$-Ga-H_2 system was used to grow GaAs epitaxial layers on GaAs substrates.

The materials used for the construction of the system are: high purity synthetic quartz /Spectrosil, Heraeus GmbH/ for the reactor tube, gallium boat, liner tube and substrate holder, $AsCl_3$ and H_2 input and bypass lines were made from pyrex. Teflon pyrex valves, and stainless steel connector parts with teflon sealings were used to make the reactor leakage free. High purity starting materials as 6N Ga /Aluminium Work, Ajka/, 5N $AsCl_3$ /M.C.P. England/ and electronic grade H_2 /Linde, BRD/ were applied. Substrate materials were n-type tellurium and tin doped LEC grown GaAs crystals /$n = 2 \cdot 10^{18}$ at/cm^3/ or chromium doped / $\varrho \geq 10^6$ ohm.cm/ semi-insulating wafers oriented 3° off (100) towards (110). The surfaces of the substrates were polished chemically, and etched in 3 H_2SO_4 : 1 H_2O_2 :1 H_2O solution at room temperature and rinsed in deionized water and electronic grade methanol.

The temperature of the Ga/GaAs source and the deposition region respectively were 823°C and 745°C regulated within $\pm$ 0.5°C accuracy by MFKI regulators. The temperature gradient in the deposition zone was 6°C/cm. To avoid the uncontrolled growth condition associated with GaAs depletion in the crust of the Ga source each run was preceded by a source saturation

cycle, while a vapour etching was carried out. The etching process took place using second bubbler from which $AsCl_3$ vapour was introduced into the deposition zone. Average growth rates were 10-12 /um/h and the $AsCl_3/H_2$ mol fraction was changed between $1 \cdot 10^{-3}$ - $2 \cdot 10^{-2}$.

In Table 1. the carrier concentration and Hall mobility of the undoped layer at room temperature and at 77 K are listed.

Table 1.

1	2	3	4	5	6	7	8
GB-35	n	4.4×10^{15}	5.3	4040	8.16×10^{15}	16300	5.5×10^{15}
GB-46	n	1×10^{15}	1.8	-	-	23360	8.3×10^{14}
GB-50	n	6×10^{15}	6	4560	2.4×10^{16}	10040	1.8×10^{16}
GB-54	n	6×10^{15}	4.6	6080	7.9×10^{15}	15450	6.3×10^{15}
GB-56	n	1×10^{15}	6	4390	6.4×10^{15}	17540	4.7×10^{15}
GB-59	n	3×10^{15}	4.5	6480	7.3×10^{16}	13490	2.6×10^{15}

1 Sample No
2 Conduction type
3 Concentration /at/cm^3/ measuring by POST OFFICE PROFILE PLOTTER
4 Layer thickness /um/
5 Room temperature mobility /cm^2/Vsec/
6 Van der Pauw concentration /at/cm^3/
7 Mobility at 77 K /cm^2/Vsec/
8 Concentration at 77 K /at/cm^2/

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SPECIAL SEMICONDUCTOR LIGHT SOURCES FOR MEDICAL APPLICATION

T. Görög J. Pfeifer
E. Lendvay

Selective spectroscopy is one of the emerging fields of interest. Using semiconductor light sources characterized by narrow band-width and high intensity, sensitive optical methods which are able to facilitate the determination of different materials, have been developed in the analytical practice. The medical application of these methods has a great importance enabling the "in situ" determination of some important biological materials. Examining the spectral ranges of interest there is a region between the visible and the near IR in which no conventionally produced LED-s or semiconductor lasers are available. Thus, suitable light sources with emission maxima between 750-900 nm and a half-width less than 60 nm have to be developed. It is known that in ternary $A^{III}B^{V}$ compounds the emission maxima can strongly be affected by the composition of solid. Therefore, for the mentioned purposes $Ga_{1-x}Al_xAs$ and LPE growth were chosen.

For LPE the constant cooling rate method and the horizontal slider technique were applied, growing one or more successive epitaxial layers on (100) oriented GaAs substrate. This method is widely used for preparation of LED-s and lasers. Its disadvantage is, however, that owing to the segregation effects the mole fraction of AlAs is not uniform, and decreases continuously within the layer. The position of the injection emission band depends on the composition of the solid at the site of the p-n junction, so the dependence of the injection luminescence in the $Ga_{1-x}Al_xAs$/GaAs system on the growth conditions /prebaking, initial temperature, cooling rate, supercooling, etc/ and on the initial liquid /source/ composition as well as the doping have been investigated. In the single-layer system Si, in multilayer structures Ge, Si, Zn and Te were used as

dopants. Alloy compositions were measured by photoluminescence as well as by electron- microprobe. The epitaxial layer thickness and the junction depth were determined after cleaving the crystal using chemical development of the layers and photomicroscopy or SEM techniques. The individual chips were made by contacting the $Ga_{1-x}Al_xAs$/GaAs wafers by AuGe, AuGeNi, AuBe and Al. The cleaved chips were mounted epitaxial side up using AuGe eutectics on a To-18 header. It was observed that at 20-100 mA dc the radiance of LED-s was sufficiently high, and that although the technology is very simple with Si doping and the spectral position can be regulated easily with composition, the necessary half-width can only be reached with multilayer /at least two-layer/ systems, using different dopants for the p and the n side. The characteristic spectra of the developed, special LED-s are shown in Figure 1.

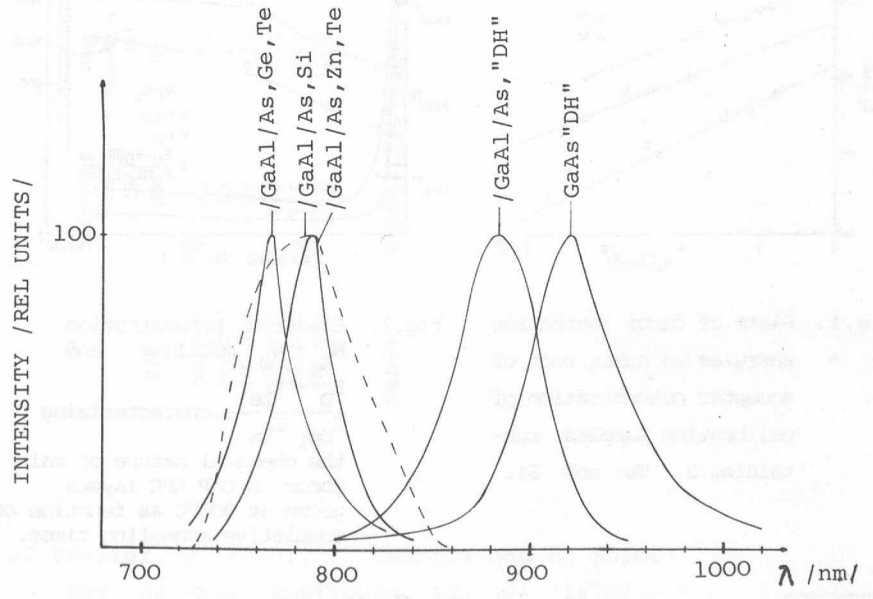

Fig.1.

OBSERVATIONS ON RESIDUAL DONORS IN GaP LPE

J. Pfeifer
B. Pődör [x]
L. Csontos
N. Nádor

Electron and donor concentrations and mobilities of non-doped liquid phase epitaxial GaP layers were studied[1] when varying the annealing process prior to growth. Main donors or the presence of more than one kind of donors were identified by donor ionization energies. /Fig.1/. After short annealings the incorporation of sulphur, after long annealings the incorporation of silicon were observed. /Fig.2., Table I./

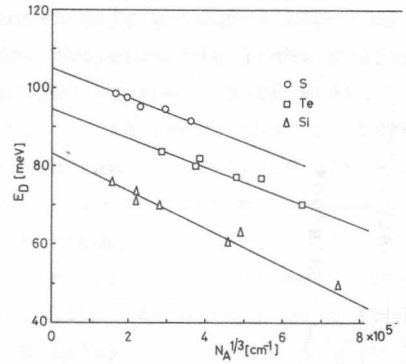

Fig.1. Plots of donor ionization energies vs cubic root of acceptor concentration of calibrating samples containing S, Te and Si.

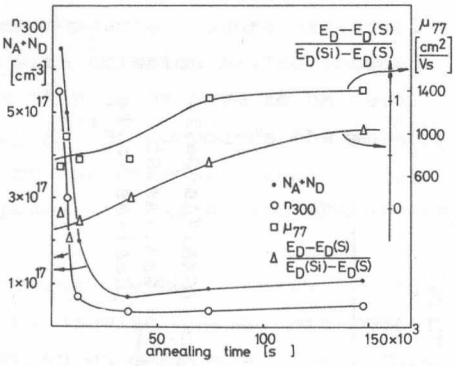

Fig.2. Electron concentration $N_A + N_D$ mobility and $\frac{E_D - E_{Ds}}{E_{DSi} - E_{Ds}}$, characterizing the chemical nature of main donor in GaP LPE layers grown at 900°C as function of cumulative annealing times.

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[x] Present address: Hungarian Academy of Sciences, Research Lab.for Inorganic Chemistry, H-1502, Budapest, P.O.Box 132

Table I. Annealing times and electrical data for growths at 990 °C

Run No	Annealing time $\times 10^3$ (s)	Annealing time *cumulative* $\times 10^3$ (s)	n_{300} $\times 10^{17}$ (cm^{-3})	μ_{77} ($cm^2/V\,s$)	E_D (meV)	N_D $\times 10^{17}$ (cm^{-3})	N_A $\times 10^{16}$ (cm^{-3})
—	—	—	—	—	—	—	—
NK 0321	4.2	4.2	5.5	702	92	6.0	5.0
NK 0607	1.8	7.8	3.0	990	102	4.9	1.1
NK 0608	4.8	12.6	7.0	760	95	1.6	4.5
NK 0619	12.0	36.6	3.7	756	95	0.59	0.93
NK 0628	37.8	74.4	3.5	1 350	85	0.70	2.0
NK 0703	73.8	148.2	4.9	1 400	74	0.88	2.2

The connection of sulphur contamination in undoped GaP LPE layers with sulphur traces of the graphite boat has been demonstrated experimentally. A decrease of the sulphur level in epi layers has been shown when annealing the boat contact with gallium.

Parallel to the decrease of sulphur level an increase in $N_D + N_A$ and a decrease in E_D connected with the incorporation of silicon has been observed.

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COMPLEX INVESTIGATION OF OXIDATION PROCESSES ON REAL III-V COMPOUND SEMICONDUCTOR SURFACES

M.Somogyi

Different types of surface treatments are an important part of semiconductor technology. Although the most ancient of them is chemical etching, it is still widely used. The most successful prescriptions and procedures are results of empirical observations, and little is known on atomic scale about the structural characteristics of an etched real surface.

Traditionally, only the freshly etched surface is regarded clean; and storage in the ambient for some hours is supposed to result in oxygen contamination as a consequence of chemical reaction between surface atoms and oxygen. In this picture several facts are postulated.

1. The existence of a surface region or layer where substrate atoms are able to react with oxygen at moderate temperatures.

2. Within this layer the atomic order of the substrate is no more preserved

3. The state of the surface layer is not stable in time, oxidation or other structural changes may proceed continuously.

In the present case this picture was used as a starting point. An outline of problem-setting and of methods used is presented in Table I.

Table 1

Subject of investigation	Method of investigation	Ref. No.
Layer thickness	Ellipsometry	1
Qualit.and quant. analysis of the surface layer	Rutherford backscattering /RBS/	2 3
Structural characterisation	Electron diffraction /ED/ Electron microscope /EM/	
Rate, direction of changes in time	Ellipsometry, RBS, ED	4

Results:

As a model material /100/ oriented GaP slices were used as most suitable to RBS[3]. The most detailed studies were carried out on surfaces etched by aqua regia[5].

Immediately after etching the presence of a transparent surface layer /1-2 nm/ could be stated by ellipsometry; and the thickness-increase in time was followed for six months /4-6 nm/. The amount of disordered substrate atoms and oxygen atoms was measured by parallel RBS determinations and was expressed as number of atoms/cm^2. The values extrapolated to the 10^{th} min. after etching were found to be:

$$Ga = 2 \cdot 10^{15}, \quad P = 2\text{-}3 \cdot 10^{15}, \quad O = 1.5\text{-}2 \cdot 10^{15},$$

increasing in six months to:

$$Ga = 3 \cdot 10^{15}, \quad P = 3\text{-}6 \cdot 10^{15}, \quad O = 5\text{-}6 \cdot 10^{15}.$$

The layer-composition in both cases is below that of the full oxide of the GaP, i.e: $GaPO_4$. From the thickness and composition data the compactness of the layers could be calculated. Results of ED and EM structural investigations are summed up in Table II.

Table II.

Structure	amorphous	microcrystalline /ϕ 10nm/
etching temp.	20-30 ^{o}C	boiling point
compactness	very low /1-2 g/cm^3/	maximal /4 g/cm^3/
conclusion /see ref.6/	high water content in the form of OH groups	almost no possibility of OH group formation
assumed mechanism of ageing	loss of water, oxidation of P^{III} to P^{V}	uptake of water from the ambient, destruction of microcrystalline structure, oxidation of P^{III} to P^{V}

Thus, for freshly etched surface layer the following tentative model can be given in agreement with the chemistry of Ga^{3+} ion in aqueous media:

ordered structure, few or no OH groups, maximal compactness ⟶ amorphous structure, OH groups present, porosity in dry state

continuous transition verified by the appropriate choice of etching temperature

It can be concluded that beside layer-composition the compactness can be regarded also as a characteristic of primary importance.

This work was carried out in cooperation with the Central Research Institute of Physics where the RBS determinations were made.

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PROMPT AND AUTOMATIC DETERMINATION OF THE DOPANT DISTRIBUTION IN III-V COMPOUND SEMICONDUCTORS

T. Sebestyen

The determination of the dopant distribution in depth or along the surface of an epitaxial layer is the most important and immediate task after the epitaxial process. This is particularly useful during a series of technological experiments for finding the best parameters of the epitaxial process.

In our institute this prompt assessment is made by a POST OFFICE PROFILE PLOTTER bought from the firm Syncryst.This equipment makes use of the fact that an interface between a semiconductor and a transparent, well conducting electrolyte behaves similar to a metal-semiconductor interface, i.e. to a Schottky diode. Thus, by measuring the capacitance, the current and the voltage informations can be obtained on the distribution of dopants and the quality of the layer. Deep profiles can be determined during a continuous etching of semiconductor by the electrolyte used.

We have successfully used this equipment /1/ for plotting the impurity profiles in GaAs VPE and LPE layers, /2/ to determine the dopant distribution along the surface of GaAs epitaxial and bulk materials, /3/ to study the influence of annealing, mechanical or chemical polishing on the dopant profile or the quality of the uppermost layer of the samples, /4/ to determine the exact position of p-n junctions, /5/ for profiling Zn diffusion tails in GaAs and GaP. In case /5/ the 10% KOH solution was superior to 0.1 M Tiron /$C_6H_4Na_2O_8S_2$/ which was generally used for assessing the semiconductor materials.

1. T.Sebestyen, E.Lendvay and T.Görög: "Quick and automatic determinaton of the dopant concentration profile of GaAs epitaxial layers."
Submitted for publ. to Acta Phys. Hung.

ELECTRICAL CHARACTERIZATION OF GaAs EPITAXIAL LAYERS GROWN ONTO A CONDUCTIVE SUBSTRATE

L. Gutai T. Görög

A new method, the angle-dependent geometrical magnetoresistance method /hereafter referred to as ØMR/ was developed in our laboratory to separate R_o, the zero-magnetic-field resistance of the active layer and R_c, the contact resistance of semi-encapsulated Gunn devices[1].

Combining this method with the usual low-magnetic-field geometrical magnetoresistance /GMR/ technique[2], it is possible now to take into account R_o, the active layer resistance rather than $R_o + R_c$, the total device resistance to calculate μ_s, the magnetoresistance mobility[3]. Without the ØMR, one of the above mentioned quantities /R_o , R_c, μ_s / has to be determined in an independent way.

Although in the case of low resistance ohmic contacts the rough supposition of $R_c \ll R_o$ leads to a relatively good result, there are some cases in which it might be principally important to seperate the bulk resistance from the contact resistance: i./ in the case of reliability studies, during an ageing process, the change of the total device resistance consists of two parts: the change of the contact resistance and the change of the mobility and/or the carrier concentration in the active layer: ii./ in the case of epitaxial layer characterisation, when the electrical parameters of an epitaxial layer grown onto a highly conductive substrate have to be measured. Due to the strong shunting effect of such a substrate, the conventional Hall or van der Pauw methods could not be applied. The usual solution of this problem is to make the electrical measurements on control wafers[4]. The electrical properties of an epitaxial layer grown onto a semi-insulating substrate could differ considerably from that of an epitaxial layer grown onto a highly conductive substrate because of the different doping content of the two substrate materials.

Using the ØMR method the electrical parameters can directly be determined on the very structure used for device production.

The further advantage of the ØMR method is its locality. Applying small area contacts the lateral distribution of the mobility, carrier concentration and contact resistance can be determined.

Since the contact resistance rises with the second power of the reciprocal contact diameter while the spreading resistance with the first one, the smaller the contact diameter the higher the contact resistance/spreading resistance ratio is. Consequently, in the case of small contacts, the contact resistance must not be neglected and the ØMR method is the only way to determine it.

In our recent paper it is shown that the total resistance of an infinite sandwich structure in an applied magnetic field can be written in the following form:

$$R_M\,/\varphi, H/ = \frac{A\,/H/}{1 + B/H/\,\cos^2\varphi} + R_c .$$

In the general case, the constants A/H/ and B/H/ depend on the magnetic field intensity only and they are highly independent of the direction of the magnetic field.

Measuring the total sample resistance R_M vs the angle φ the constants A, B, R_c can be calculated.

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THE APPLICATION OF THE DLTS METHOD IN THE INVESTIGATION OF GaAs EPITAXIAL LAYERS

B.Szentpáli

A new DLTS method has been realized[1] for the purpose of investigating GaAs epitaxial layers. On these layers microwave Schottky barrier mixer diodes were fabricated. The aim of the DLTS measurements is the search of the correlation between the noise of diodes and the deep level content of their crystals. The apparatus can measure deep levels in GaAs with ionization energies between 0.2 and 1 eV. The smallest detectable concentration rate of the deep levels and the donor atoms is $3 \cdot 10^{-3}$.

Two series of crystals can be distinguished. In epitaxial layers belonging to the first group there is no detectable concentration of deep centers. In the second class of crystals two characteristic deep levels have been found. Their ionization energies are 0.48 eV and 0.83 eV. The typical concentration rates are about 0.01 and 0.07 ... 0.1. /In the literature both of the centers are often attributed to oxygen impurity./

The noise figures of the microwave mixer diodes made on these crystals were measured in the mixer unit of a receiver system /type GTT-70/ working in the 6 GHz band. The noise figures of diodes fabricated on crystals belonging to the first group are about 4.3 ... 4.9 dB, while the diodes made on crystals containing the above mentioned deep centers show a noise figure of about 7 dB. Direct quantitative correlation between the noise and the deep levels has not been found yet.

1. B. Szentpáli: "A new DLTS method"
to be published in Acta Physica Hungarica.

STUDIES ON AGEING BEHAVIOUR OF LEDs

G. Ferenczi J. Kiss
M. Somogyi T. Temesvári
G.Aszódi

Long time degradation of the external quantum efficiency of GaAsP, GaP LEDs have been investigated by DLTS and electroluminescent methods. Commercial uncapsulated diodes were aged up to 500 A/cm^2 d.c. current density. The ageing was carried out at different temperatures up to 200°C. The results can be divided into two distinct groups:

1. Catastrophic failure:

1.1 Purple plague: The Al p-contact was bonded with gold wire. Purple plague was typically observed after 1000h operation time under normal stress condition. At elevated temperatures, however, the failure is observed much earlier. We believe, this is the first experimental observation of purple plague on GaP.

1.2 p-contact break off: In cases where too high stress was applied at thermo-compression fresh dislocations were created. The dislocation climb caused probably by recombination enhanced defect motion creates a macroscopic stress concentration leading to contact break off. The increase of the dislocation density can be monitored by the increase of the space-charge recombination current.

2. Decrease of the quantum efficiency

2.1 Deep level spectroscopy revealed the presence of a trap in $GaAs_{.62}P_{.38}$ exhibiting strongly non-exponential thermal emission and capture. The experimental facts can be explained by assuming non Shockley-Read trap behaviour: The activation energy of the centers depends on the occupation number. An extended defect where the build-up of a re-

pulsive electrostatic field is possible seems to be an excellent candidate to explain the experimental results. The concentration of this trap depends linearly on the increase of the number of the non-radiative spots /dark spots/.

2.2. As an other example of the recombination enhanced defect motion we observed the dissociation of the nearest neighbour Zn-O pairs. The decreased activation energy of the pair dissociation indicates the ratio of the radiative to non-radiative component of the recombination process.

1. G. Ferenczi: "Physical sources of the ageing of LED's" invited talk will be given at the RECON'79, Prague, Sept.4-7,1979.

2. G.Ferenczi: "Deep level studies on extended defects in $GaAs_{.38}P_{.62}$" talk given at the: New Development in Semiconductor Physics Meeting,Szeged, July 1-6, 1979.

THEORY OF OHMIC CONTACTS BASED ON GRADED TRANSITION LAYERS

T. Sebestyen

Semiconductor contacts with ohmic character and low specific contact resistance can be formed by decreasing the width and the height of the energy barrier due to the different work functions and/or electron affinities of the joining materials. The usual way of decreasing the barrier width is the preparation of a highly doped contact layer for promoting the tunnelling process[1].

The barrier height can be decreased by applying a graded transition between the two materials. Making the metallurgical transition wide and smooth enough good ohmic contacts can be formed for any pair of materials.

In our model of ohmic contacts based on grading two matching parabolas are used for describing the distance profiles of the compositions and the electron affinities. This approximates well an interdiffusion case. A linear approximation for the reciprocal permittivity as well as homogeneous space charge densities due to the doping, and interface states scattered over the transition layer are assumed. By solving the Poisson-equation general results in closed algebraic forms could be obtained for the distance dependence of the energy bands, the grading length belonging to the zero barrier height, the capacitance etc.[2,3].

1. T. Sebestyen, H. Hartnagel and L.H.Herron: "New design criteria of Gunn diode contacts." Inst.Phys.Conf.Ser. No. 24 /1975/ pp.77-88

2. T. Sebestyen: "Low resistance transition layers to GaAs" C.Sc. of Physics dissertation, Budapest, 1978.

3. T. Sebestyen: "Models for ohmic contacts and graded crystalline or amorphous heterojunctions" Prepared for publ.in Solid-State Electr.

THE DEVELOPMENT OF MICROWAVE MIXER SCHOTTKY BARRIER DIODES

B. Szentpáli A. Andrási
Á.Tichy-Rács

In recent years the technology of metallization of ideal metal-GaAs /Schottky barrier/ contacts was developed in our institute. On the basis of this work microwave mixer diodes were prepared in 1978. In the present report the main technological steps and the measured noise figures characteristic of the diodes are described.

In the chip technology /Fig.1./ the GaAs epitaxial layers are covered with a SiO_2 layer to avoid the surface leakage current causing a higher noise level. An about 1 /um thick SiO_2 layer is deposited by CVD technique from silane at 450°C. Using a photoresist film /Shipley AZ-1350/ windows are formed in the SiO_2 layer. Before the vacuum evaporation of metals the GaAs surface is once more cleaned chemically. The metallization consists of a Cr layer with a thickness of about 0.1 /um and an 0.15 ... 0.2 /um thick layer of Au on it. The Cr is the barrier metal and the Au layer protects it from oxidation and makes easier the thermocompression bonding. After the metallization the photoresist layer is lifted off and the back side of the wafer is alloyed by Au:Ge eutectic to reach good ohmic contact. Diodes with 6 ... 10 /um diameters have been prepared this way. The structure is controlled by scanning electron microscopy /Fig.2./.

The diode chips are mounted onto microwave diode headers type S4. The active area of the diodes a 7.5 /um Au wire is contacted by thermocompression.

The diodes were tested in the mixer unit of a receiver /type GTT-70/ in the 6 GHz band. The noise figure of the diodes depends, first of all, on the quality of the GaAs epitaxy. The noise figure of the best diodes of our series in 1978 is 4.3 dB, and the typical values are in the range from 4.5 to 4.9 dB.

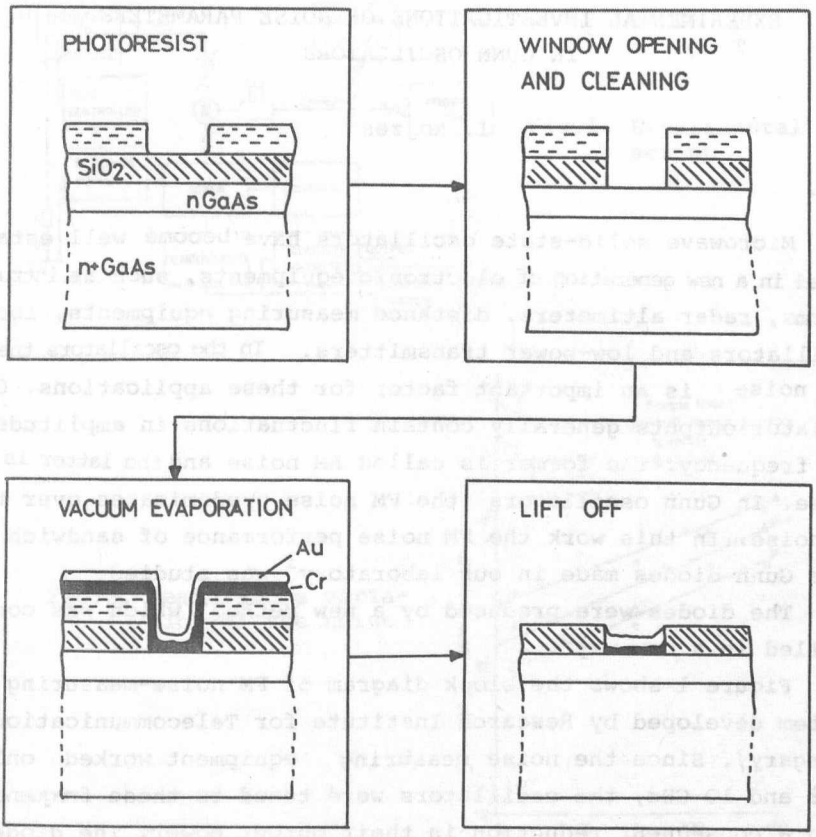

Fig.1. The main technological steps of diode fabrication

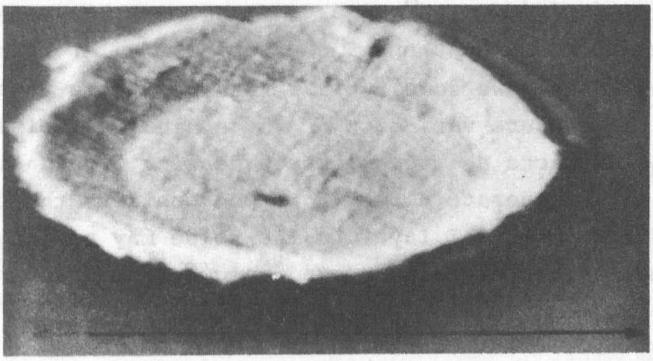

Fig.2. The scanning electron micrograph of a mixer diode. The diode is tilted by an angle of 60^{o}.

EXPERIMENTAL INVESTIGATIONS OF NOISE PARAMETERS IN GUNN OSCILLATORS

I. Mojzes

Microwave solid-state oscillators have become well established in a new generation of electronic equipments, such as intruder alarms, radar altimeters, distance measuring equipments, local oscillators and low-power transmitters. In the oscillators the low noise is an important factor for these applications. Oscillator outputs generally contain fluctuations in amplitude and frequency. The former is called AM noise and the latter is FM noise. In Gunn oscillators the FM noise predominates over the AM noise. In this work the FM noise performance of sandwich type Gunn diodes made in our laboratory[1] was studied.

The diodes were produced by a new method[2] which was controlled in a new way[3].

Figure 1 shows the block diagram of FM noise-measuring system developed by Research Institute for Telecommunication /Hungary/. Since the noise measuring equipment worked only at 8 and 10 GHz, the oscillators were tuned to these frequencies with a consequent reduction in their output power. The diode under test was placed in a temperature stabilized coaxial cavity. In the cryostat containing the cavity the temperature was controlled with an accuracy of $\pm$ 2°C in the range of - 60 ... +100°C using an oscillating Gunn element developed in our institute.

Figure 2 shows some typical results of the investigations of the temperature variation of the equivalent noise voltage.

The contacts and the electron density fluctuations in epitaxial layer generate noise. For good contacts the contribution of the epitaxial layer to the noise may no longer be negligible. Further experiments and calculations are in progress.

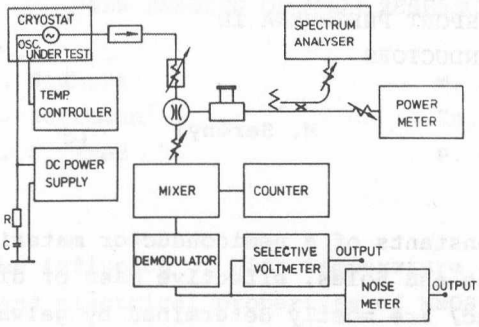

Fig.1. Experimental set-up

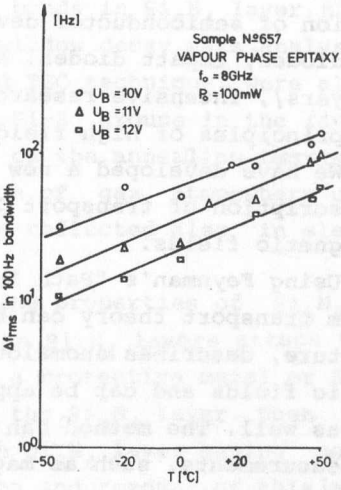

Fig.2. Temperature variation of the noise

1. I. Mojzes, A. Barna, B.P. Barna: "Technological optimization of GaAs Gunn diodes" Proc. of the 6th Coll. On Microwave Commun., MICROCOLL'78, Budapest /Hungary/, Vol. II., pp. V-2 /10.1-10.4/1978/

2. A.Barna, F. Beleznay, I. Mojzes, B.P.Barna, Gy. Stark: Hung.pat. application No.MA-2718

3. I. Mojzes,"Formation of AuGe contacts to n-GaAs" Phys. Stat.Sol. /a/, 47, K183-185 /1978/

HIGH FIELD TRANSPORT PHENOMENA IN SEMICONDUCTORS

F.Beleznay M. Serényi

The most important constants of a semiconductor material /concentration of electrons and holes, effective mass of different charge carriers etc./ are mostly determined by galvano--magnetic measurements. During the last decade, following the invention of semiconductor devices using high local fields /Gunn diodes, Impatt diodes, MOS structures with thin insulating layers/, intensive research has started to understand the basic principles of high field galvano-magnetic phenomena.

We have developed a new theoretical method which allows the description of transport phenomena both in high electric and magnetic fields.

Using Feynman's "Path Integral" method a new consistent quantum transport theory can be derived which, first in the literature, describes anomalous mobility in high electric and magnetic fields and can be applied in the classical and quantum limit as well. The method can be applied for nonstandard transport measurements, such as magneto-phonon resonance,too.

1. F.Beleznay and M.Serényi:"Application of a new high field quantum magneto-transport theory for polar semiconductors" Solid-State Electronics 21,215 /1978/

2. F.Beleznay and M.Serényi: "Application of a new quantum transport theory I: perturbation expansion for high field magneto-transport"
To be published in J. Phys.C.

NEW RESULTS OF MNOS RESEARCH

G. Stubnya
G. Hoffmann+
I. C. Szép
M. Andrási
Zs. Horváth
P. Tüttő

The influence of high temperature annealing on the structural and electrical properties of MNOS memory structures has been studied using multiple internal reflection /MIR/ spectroscopy to determine the N-H and Si-H bonds in Si_3N_4 layer. Electrical methods, such as the memory window decay rate, analysis of memory hysteresis, C-V curves and TSC technique, were also applied. Distribution of N-H and Si-H groups in the layer showed a strong dependence not only on the annealing temperature and time but also on the composition of gas atmosphere used during annealing. These changes were reflected also in electrical data.

Work was performed on the etching properties of Si_3N_4. Etching solutions applied to etch the Si_3N_4 layers attack the photoresist layers, too. Therefore, a protective metal or SiO_2 layer was deposited onto the top of the Si_3N_4 layer. When fabricating MNOS memory devices with Si_3N_4 layer having not only a protective role, the deposition and removal of this layer may have a detrimental effect on the memory characteristics. We made experiments in different gas atmospheres after growing nitride layers to convert the top layer into oxide.

The effect of these annealing cycles on memory characteristics has been investigated. A suitable procedure was established concerning both the electrical and etching properties.

Considerable effort has been devoted to study the hysteresis behaviour known since 1968 in MNOS structures. Frohman-Bentchkowsky and Lenzlinger calculated theoretical hysteresis

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+Division of Optics and Electronics

curves for MNOS structures with comparatively thick oxid layers /5nm/. Despite this there is no published method of evaluation to obtain information from experimental hystersis curves. We have developed a new method which seems to be useful to evaluate such hysteresis curves from the slope, the width and the asymmetry of the hysteresis curve. By this method informations on the conductivity of insulator layers, the fixed charge density in the vicinity of the Si-SiO_2 interface and the efficiency of charge injection can be obtained.

1. G.Stubnya, I.C. Szép, G. Hoffmann, Zs. Horváth, P.Tüttő: "Distribution and role of N-H and Si-H bonds is MNOS structures" Presented at the 8th ESSDERC Published in Revue de Physique Appliquée 13. 679-682, /1978/

2. M. Andrási, G. Stubnya: "The possibilities of etching patterns in Si_3N_4 layers" /in German/ Presented at the Microelectronics Conference, Dresden, GDR 1978.

3. Zs. J. Horváth: "Evaluation of the hysteresis of MNOS memory elements" /in Russian/ Presented at the 23rd Intern. Scient. Colloquium, Illmenau, GDR, 1978. Published in the Conference Proceedings, Part 7., pp. 81-84

DEVELOPMENT AND CHARACTERIZATION OF CCD DELAY LINES WITH OVERLAPPING POLYSILICON AND ALUMINIUM GATES

S. Biró
G. Forgács
M. Németh-Sallay
J. Selmeczy

Four phase 32-bit charge-coupled device /CCD/ shift registers with overlapping polysilicon and Al gates were designed and fabricated. The structure of the devices is shown in Fig.1, while the photomicrograph of the chip containing one 32-bit and three smaller test CCD's is shown in Fig.2.

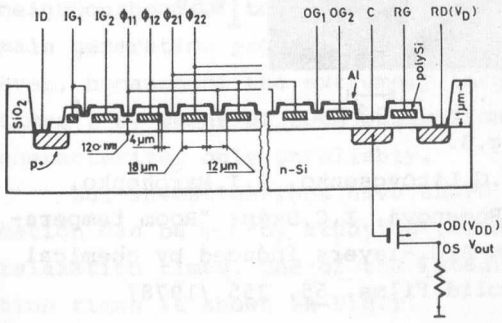
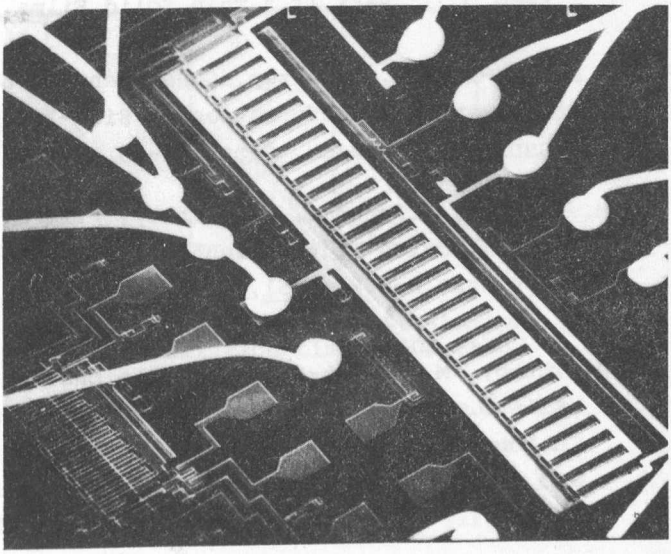


Fig.1.

In relation to the technological process the effects of various treatments on the oxide and Si/SiO_2 interface properties were investigated[1-5]. The investigation of the effect of boron doping and subsequent oxidation of polysilicon on the device characteristics is still in progress.

Fig.2.



The CCD's were driven by 2-phase clocks and exhibited efficient shift register operation for both digital and analog signals at clock frequencies 20 kHz to 2 MHz with output signals of 0.5-1.0 V.

The delay of an analog signal by the 32-bit CCD is demonstrated in Fig.3. at f_c = 80 kHz. The devices showed also an excellent light sensitivity, so they are prospective photodetecting devices.

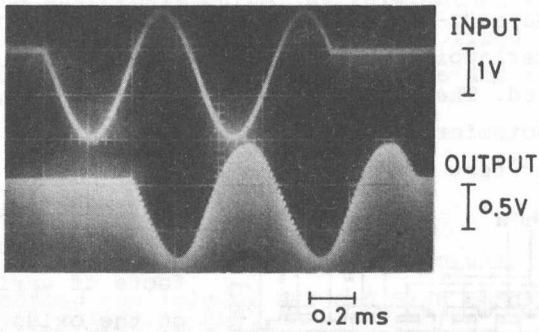


Fig.3.

1. A. Barna, P.I.Didenko, V.G.Litovcsenko, P.I.Marchenko, M.Németh-Sallay, G.F.Romanova, I.C.Szép: "Room temperature transformation in SiO_2-layers induced by chemical compounds I.," Thin Solid Films, 55, 355 /1978/

2. G. Hoffmann, A. Lőrinczy, M.Németh-Sallay, I.C.Szép: "Room temp. .... Part II." Thin Solid Films, 59, 319 /1979/

3. M.Németh-Sallay, I.C.Szép, G.Hoffmann, A.Lőrinczy: "Room temperature transformation in SiO_2-layers...." ESSDERC'78, France, Sept. 11-15, 1978. Abst. p.398

4. M. Andrási, G.Forgács, A.Lőrinczy: "The effect of potassium contamination of tungsten on filament metallized devices" Phys.Stat.Sol. /a/ 51, 573 /1979/

5. P. Tüttő, M. Németh-Sallay: "The characteristics of Si-SiO_2 interface by minority carrier lifetime inhomogeneity measurements on MOS capacitors" 23.Int.Wiss. Koll., 1978. Heft 7., pp. 21-24

MINORITY CARRIER LIFETIME STUDIES IN MOS STRUCTURES

P. Tüttő

The measurement of minority carrier lifetime by impulse C/V/ method is one of the most widely used methods in the study of MOS structures. Charge generation processes can be studied by this method giving information on the most important regions of devices. This very sensitive method can directly qualify the neighbourhood of the $Si-SiO_2$ interface. In certain cases the main generation processes are difficult to be determined, however, because of the extremely large dispersion of relaxation times[1]. By means of such relaxation times the slices can be characterized only unreliably.

Our investigations have shown that more resonable information can be got by studying the distributions of the measured relaxation times. One of the integral distributions of relaxation times is shown in Fig.1.

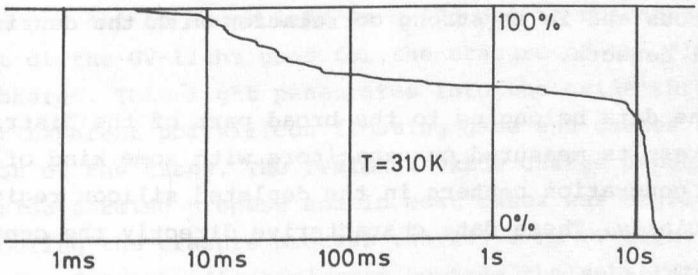


Fig.1. Measured integral distribution of relaxation times /100 data/

These distributions have generally two parts. One of them occurs at high lifetimes and its dispersion is about 10 %. The other with an extremely broad dispersion of about one order of magnitude takes place at much smaller lifetimes.

The slices can very often be characterized by this distribution. Measuring a number of samples the shape of the two parts were found not to be changed. There were only differences in the amplitude of the parts and in the mean values.

Having studied the distributions of relaxation times the following conclusions can be drawn:

1. The separation of the distribution into two parts can be attributed to macroscopic centers, especially to stacking faults.

2. The data belonging to the small dispersion part are results measured on capacitors having an active silicon region free from macroscopic defects. The mean value of this part does not change significantly over the slice. The determination of this value is useful, however, for much more reliable qualifying of the technology. The separation of the volume and the lateral /surface state/ processes is possible by measuring the distributions of two or more types of capacitors on the same slice.

3. The rate of the amplitudes of the two parts characterises the density of macroscopic generation centers. It is laterally inhomogeneous and is in strong correlation with the density of structural defects.

4. The data belonging to the broad part of the distribution are results measured on capacitors with some kind of macroscopic generation centers in the depleted silicon region or in its vicinity. These data characterize directly the centers.

Taking into account the distribution of relaxation times it is possible to determine the dominant minority carrier generation processes and to give a more detailed quantitative description of the minority generation behaviour of slices.

1. P. Tüttő, M.Németh-Sallay: Paper presented at 23rd Int. Sci. Coll. Techn. Hochschule Ilmenau, 1978.

THE DEGRADATION POSSIBILITIES IN FAMOS MEMORY DEVICES

A. Lőrinczy Yu. Ponomarenko

The writing of the Floating Gate Avalanche Injection Metal Oxide Semiconductor /FAMOS/ memory devices means a charging of the floating gate and a formation of a channel between source and drain. The writing of the p-channel FAMOS is accomplished by hot electrons sweeping from the avalanching drain junction to the floating gate through the oxide. A part of these electrons is trapped in a region of the oxide above the drain p^+-n junction, lowering both the junction breakdown current and the oxide /writing/ current. Due to this effect an undesirable elongation of the writing time takes place. /To minimize this effect an oxide with small trap concentration must be used i.e. an oxidation by dry O_2 is advantageous/. The more times the writing is repeated the more charge in the oxide can be trapped resulting in more difficult writing. Our devices, however, showed no significant change in the duration of the writing time after multiple writing[1]. The trapped charge turned out not to accumulate in oxide due to the annealing effect of the UV-light used for the erasure of the floating gate charge. This light penetrates into the oxide through the semitransparent polysilicon floating gate and causes a depopulation of the traps. The residual oxide charge depended on the oxide forming process and in most cases was negligible.

During the erasure process the 253,7 nm UV-light emmits electrons from the floating gate towards the substrate, and below the total area of the gate the oxide traps become filled. The photoemission current is limited by trapped charge and the erasure decelerates with every cycle. For reliable erasure generally long erasure time /15 min/ is recommended. If the trapped charge value is high, a channel can be induced between the drain and the source, even if no charge was written on the floating gate. The possibility of this phenomenon was investi-

gated in details on biased MOS capacitors irradiated by UV-light for a long time for totally filling the traps. The shift of the flat-band voltage was less than 100 mV for all investigated types of oxide, thus the trap concentration was smaller than $1,5 \cdot 10^{15}$ cm^{-3}. Much larger trap concentration was found in the same capacitors in case of avalanche-produced trapping. All these mean that UV-light both fills and depopulates the traps at the same time, and the trapping saturates at lower value. Such a little shift of the flat-band voltage is not dangerous for a memory device because it cannot change the logical state of the FAMOS.

Recently we have observed a new possibility of the erasure degradation. A long time UV-irradiation caused a crystallization of the phosphosilicate glass /PSG/ of the chip. Growing over the floating gate the non-transparent crystals can cut off the UV-light and block the erasure. This effect was observed in case of heavily doped PSG.

The loss of the stored charge in an ideal case is determined by the Fowler-Nordheim tunnelling through the 120 nm thick oxide layer. The loss can be increased by additional conductivity mechanisms related to the chemical changes in the oxide which can appear due to the UV-irradiation, the high density of the trapped charge and the application of a strong electric field during device operation. Beside these, shortly after writing a positive charge accumulates at the substrate-oxide interface, shielding partially the effective negative charge of the floating gate. We have observed that the multiple repetition of the writing-erasure cycle /about 150-200 times/ caused no significant change of the charge retention curves, unless the device get totally damaged. Moreover, at some slices the initial decay of the retention curve in the first 10-50 hours was made smaller in such a way. Probably, the annealing effect of the UV-irradiation decreased the number of the positive interface states.

1. F.Heksch, A.Lőrinczy and Yu.Ponomarenko: paper presented at the Microelectronics Elements Conference, Dresden, Oct. 1978.

RESEARCH AND DEVELOPMENT OF ACOUSTIC SURFACE WAVE DEVICES

M. Andrási
F. Beleznay
S. Püspöki
M. Serényi

In piezoelectric materials coupled acoustic and electric waves propagate. Typical velocity of this coupled mode is the sound velocity. Waves of this type,i.e. surface acousto-electric waves /SAW/, propagating at the surface can be generated, formated and detected by suitable interdigital transducers /IDT/ at the surface of the piezoelectric substrate. According to the sound to light velocity ratio typical dimensions of a particular SAW device are less than 1 cm which allows a convenient formation, filtering in the high frequency /10-1000 MHz/ range. The advantages of SAW devices are demonstrated on a TV IF filter developed in our laboratory. Conventional LC filters which have been used as TV IF filters previously consist of several coils to be adjusted. Recently, however, cost-saving simplification in the TV set has been promoted rapidly by adopting MSIs, and adjustment procedures in assembly lines have been remarkably reduced. Desired filter response is now realized easily by advanced SAW filter design technique. We have developed and applied a new filter design method which can be applied for filters with highly asymmetric amplitude response and variable group delay time. Structure of the SAW filter is shown in Fig.1. Fig.2. shows the input interdigital transducer of a TV IF filter. The calculated and measured amplitude and group delay responses are compared on Figs. 3. and 4.

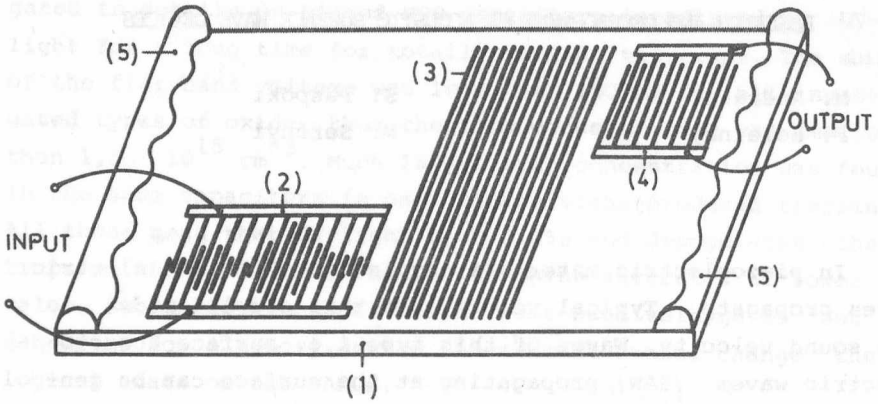


Fig.1.

/1/ Piezoelectric substrate /$LiNbO_3$/;
/2/ Input IDT; /3/ Multistrip coupler; /4/ Output IDT;
/5/ Absorber

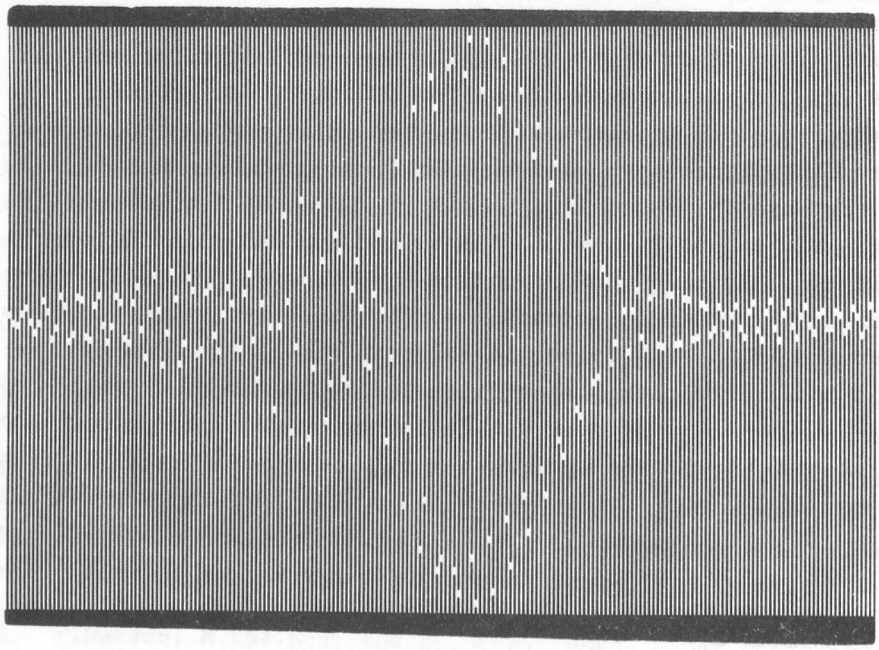


Fig.2.

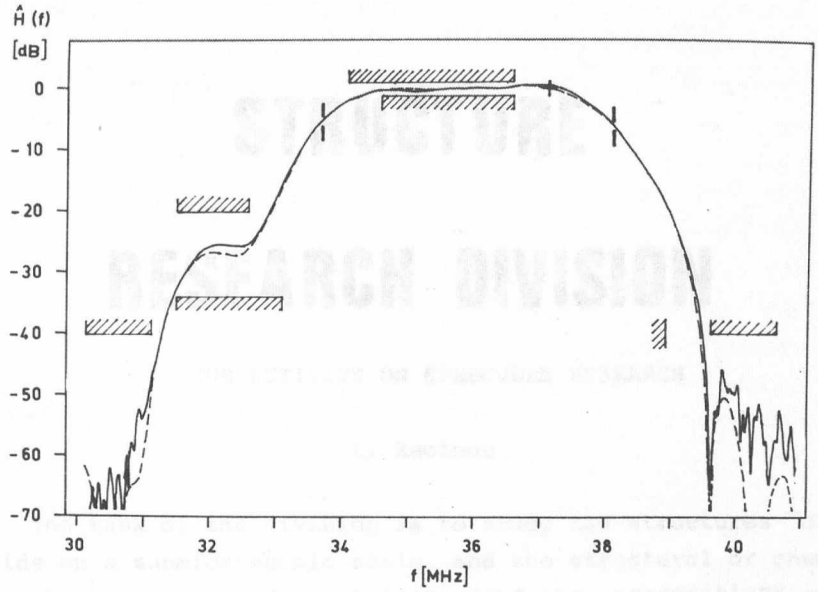
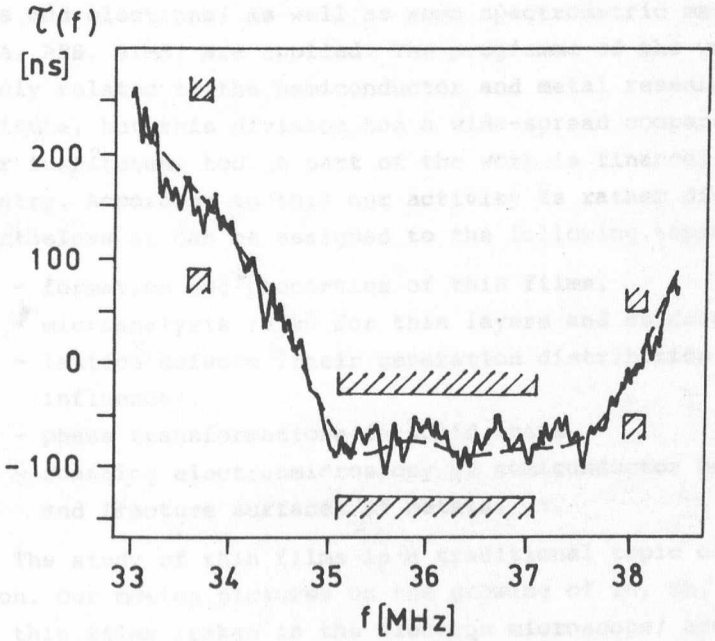

Ĥ (f)
[dB]
0
-10
-20
-30
-40
-50
-60
-70
30
32
34
36
38
40
f[MHz]

Fig.3.


τ(f)
[ns]
200
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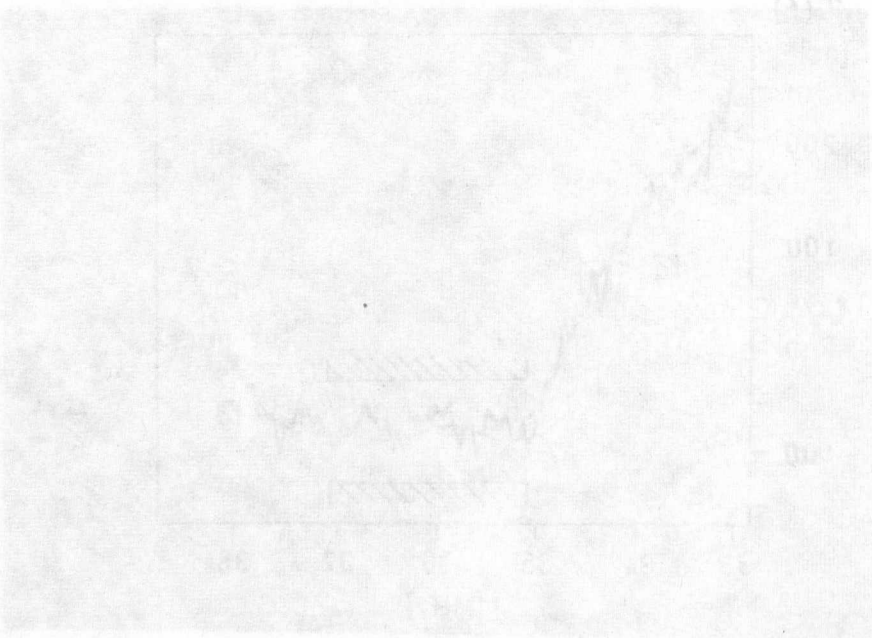
0
-100
33
34
35
36
37
38
f [MHz]

Fig.4.



STRUCTURE

RESEARCH DIVISION

OUR ACTIVITY ON STRUCTURE RESEARCH

L. Zsoldos

The task of the division is to study the structures of solids on a submicroscopic scale and the structural or chemical inhomogeneities of the lattice /defects, segregations etc./ For this purpose diffraction and imaging techniques /using X-rays and electrons/ as well as some spectrometric methods /EPMA, AES, SIMS/ are applied. The programme of the work is closely related to the semiconductor and metal research in the Institute, but this division has a wide-spread cooperation with other institutes, too. A part of the work is financed by the industry. According to this our activity is rather diverse. Nevertheless, it can be assigned to the following topics:

- formation and properties of thin films,
- microanalysis /also for thin layers and surfaces/,
- lattice defects /their generation distribution and influence/,
- phase transformations in solid state,
- scanning electronmicroscopy of semiconductor devices and fracture surfaces of metals.

The study of thin films is a traditional topic of our division. Our motion pictures on the growing of In, Sb, Ge, Al, etc. thin films /taken in the electron microscope/ are well known for many scientists all over the world. In the last years a special sample holder has been developed which ensures

10^{-6} - 10^{-5} Pa around the sample and enables electrical measurements and heating or cooling of the sample during the "in situ" observation of the growth process. The intention of the recent work is to study the role of impurities on the structure and properties of thin films.

The microanalysis is a result of the development of the last few years. One of the forthcoming papers illustrates the facility given by the conventional transmission electron microscope equipped with a wavelenght dispersive spectrometer. Auger electron spectroscopy on fracture surfaces of steel and tungsten wires was applied to study second phases and grain boundary segregation. The secondary ion mas spectroscopy has also been introduced recently. Its application is going on.

For the study of lattice defects both the electron beam methods and the X-ray topography are successfully applied. A small series of double-crystal X-ray topographic goniometers was constructed and built in the Institute. Three of them are working in other laboratories.

The study of phase transformations and the phase identification is based on X-ray and electron diffraction including high temperature work. In some cases the determination of the crystal structure should also be made. A part of the results of this work is reported in this yearbook /p. 21 / .

The scanning electron microscopy is the newest field of our activity. The work started at the beginning of 1978. At present these studies are carried out in most cases in cooperation with other institutions.

The division has a scientific cooperation with the following foreign institutes.

Central Institute of Electronphysik of the Acad.Sci.of GDR,Berlin

Central Inst.of Physics, Institute of Physics and Materials Techn., Bucharest

Department of Mineralogy, L.Pasteour University Strasbourg

Department of Physics, Phillips University, Marburg

Institute of Crystallography of the Soviet Acad.Sci.Moscow

Institute of Physics of the Polish Acad.Sci. Warsaw

Institute of Semiconductor Physics of the Siberian Branch of the Soviet Acad.Sci., Novosibirsk

Institute of Solid State Physics and Electronmicroscopy of the Acad.Sci. of GDR, Halle

Laboratory of Optics of Solids, U.of Paris VI, Paris

Our papers published in 1978 in foreign language and not included in the references of the relevant papers of this yearbook are:

1. A.Barna, P.B. Barna, A. Belu, A.Dévényi, Gy.Radnóczi,P.Thomas and L.Tóth:"Remarks on the real structure of amorphous thin films" 9th Hungarian Diffraction Conf. 1978. p.3

2. A. Barna, P.B.Barna, Gy.Radnóczi, H.Sugawara and P.Thomas: "Computer simulation of the post-nucleation growth of thin amorphous Ge-films" Thin Solid Films 48, 163 /1978/

3. A.Barna, Gy.Stark: "Analytical determination of the potassium content of single bubbles in annealed tungsten wires" Metallurgical Transactions A 9, 595-96 /1978/

4. P.Gács, M.Farkas-Jahnke, I.Szép and K.Vadasdi: "On the structure of /piezoelectric/ $Pb_2Bi_{24}O_{38}$" Acta Cryst. A34 Part S4 368 /1978/

5. Gy.Gergely, M.Menyhárd: "Auger electron spectroscopy of some impurities affecting mechanical properties of metals" Proc. 7th Congress on Material Testing, Scientific Society of Mechanical Engineers, Budapest, 1978. 2, p. 943

6. Gy.Gergely, M.Menyhárd: "On the decomposition of thin insulator films under electron bombardment". Acta Univ. Wratislaviensis No. 439, Matematika,Fiziyka, Astronomia XXXI. 91-99 /1978/

7. T.Grósz, M.Farkas-Jahnke, E.Benes, K.Vadasdi: "On the structure and decomposition of ammonium-metatungstates" Acta Cryst. A34, Par S4 S374 /1978/

8. F.M.Helmi, A.Cziráki, B.Fogarassy,L.Zsoldos and V.Eigner: "Phase transformations in cold worked Cu-8Ni-5Sn during thermal aging" Acta Cryst. A34 Part S4 279 /1978/

9. A.Kele, L. Uray, I.Gaál and M.Menyhárd: "State of bonding and distribution of impurities in K-Al-Si doped tungsten wires" Plansee Berichte für Pulvermet. 26, 3 /1978/

10. R.Manaila, C.Rusu, A.Dévényi,A.Barna, P.B.Barna, Gy.Radnóczi, and L.Tóth: "Structure studies on two component /Mo-Ge/ amorphous cermet films" 9th Hungarian Diffraction Conference 1978. p.S5

11. M. Menyhárd:"Investigation of cleaved surface of tungsten wires by Auger electron spectroscopy" ECOSS I. 1978.Abstr.220

12. M.Menyhárd: Determination of grain boundary segregation". Scripta Met. 12, 499 /1978/

FORMATION OF ALUMINIUM THIN FILMS IN THE PRESENCE OF OXYGEN

A. Barna
P.B. Barna
G. Radnóczi
F. M. Reicha[+]
L. Tóth

Aluminium thin films prepared by vacuum evaporation are frequently applied in various industrial products.It is well known that film properties are associated with film structures and they can be realised by choosing appropriate preparation techniques and parameters. Aluminium films deposited by a given technology have characteristic grain structures. The lateral grain size distribution has two maxima at significantly different grain sizes, and some crystallites protrude above the others[1] /Fig.1./. The reasons and mechanisms of the formation of such grain structures have not been cleared up yet.

The formation of Al films in respect of the growth of crystallites was studied by the authors for a better understanding of the effects of oxygen on the structure and homogeneity of the films. Examining the structure of Al films deposited at different impingement rates /K/ of oxygen to aluminium we have found three characteristic types of grain structures. These structures continuously follow each other as the oxygen pressure increases.

If $K = 10^{-2} - 10^{-3}$ the liquid-like coalescence is not hindered.[2] Therefore, crystallites with diameter of some micrometers are formed. The increase of the film thickness takes place by layer growth of individual crystallites[3]. In this stage the oxide particles formed on the surface of the film are inhibitors for the motion of growth steps. Stopping of growth steps at certain points results in the formation of hillocks /Fig.2./. When the quantity of the adsorped oxygen is not sufficient for nucleation the oxygen molecules are dragged with the moving growth steps.

[+]Ph.D. student from University of Alexandria, Egypt

Fig.1. Surface replica from Al metallization applied in integrated circuit production

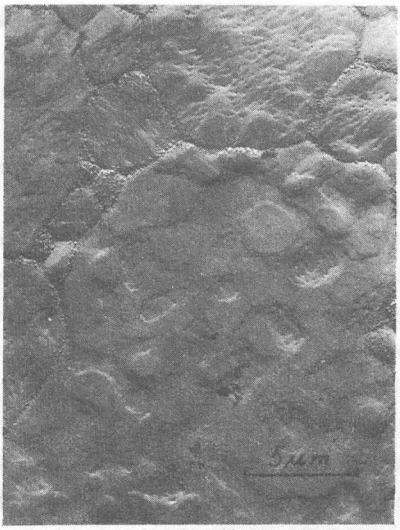


Fig.2. Surface growth structure of single crystallites of a 1 /um thick Al film deposited at 300°C, $K_{oxygen} = 10^{-2} - 10^{-3}$

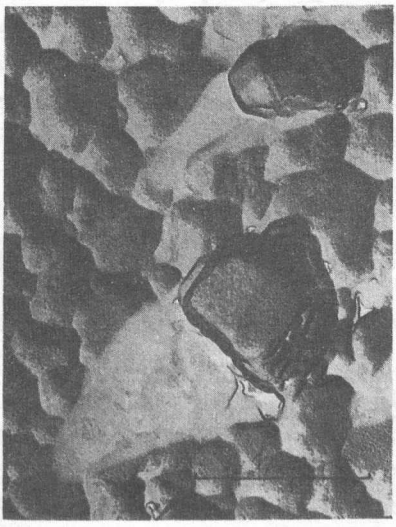


Fig.3. Surface structure of a 1 /um thick Al film deposited /at 300°C. $K_{oxygen} = 10^{-1} - 10^{-2}$

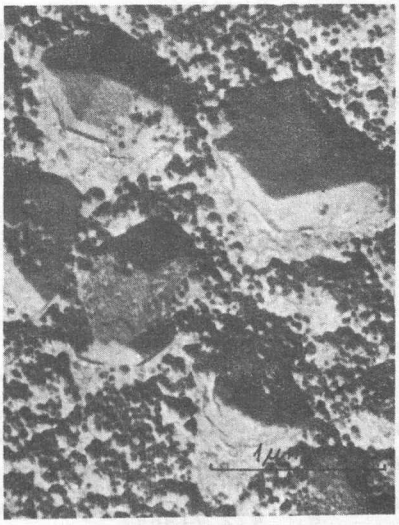


Fig.4. Surface structure of a 60 nm thick Al film deposited at 300°C. $K_{oxygen} \simeq 1$

The presence of oxygen becomes noticeable already in the stage of liquid-like coalescence when the ratio K increases.As a result the grain size becomes smaller. In consequence of layer growth and coalescence, the oxygen is drawn towards the periphery of the grains. The sticking coefficient of oxygen atoms is different on crystal planes of different indices [4], therefore the favourably oriented crystallites may grow on. This leads to the appearence of protruding crystallites having regular shape /Fig.3./. If the covering layer becomes continuous on the lateral faces they loose their regularity.

If $K \simeq 1$, the coalescence is hindered already in the first stages of grain growth. This results in a fine-grained structure. During further growth an additional maximum appears in the grain size distribution. Grains are formed with a diameter an order of magnitude larger than that of the fine grain /Fig.4 /. We suppose that the binding of oxygen is more effective in areas covered by oxide phase than on Al surfaces and Al prefers binding to Al. As a consequence certain aluminium grains having favourable orientation can start growing rapidly by collecting adatoms and atoms from the vapour beam. This is supported by the results of electron probe microanalysis: in the fine-grained areas the oxygen content was about twice as high as in the large crystallites.

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GRAIN BOUNDARY MOVEMENTS IN THINNED TUNGSTEN SPECIMENS

A. Barna P. B. Barna
G.Radnóczi

Investigations were carried out on K, Al and Si doped wires of 0.18 /um diameter. The results give information on the grain structure and on the dynamics of the structural change taking place during heat treatment as well as on the development and composition of the second phases, so called "bubbles".

Samples thinned along the wire axis of severely drawn tungsten were heat treated between 1300 and 2300 K in steps of 200 K at pressures of 10^{-3} Pa in a vacuum chamber, to study the dymanics of structural transformations. The same areas of these samples were observed by 100 kV TEM after each heat treatment.

Formation of new crystallites cannot be detected in this temperature interval. The sources of grain growth are the crystallites exhibiting lower dislocation density and double grain size with respect to others. It is possible that these crystallites were either larger originally or become larger in the sample as a consequence of the thinning procedure.

Bubbles first appear on some inhomogeneities. These can be either second phases or pores spread during swaging and wire drawing. The formation of bubbles from pores or second phases starts at 1300 K /30 s/. Also the grain boundaries get cleaner and the concentration of dislocations decreases drastically /Fig.1/.

After an additional heat treatment /1500 K, 30 s/ the dissolution of dislocation boundaries is observed with further development of bubbles from rod shape to the spherical one. At even higher temperatures bubbles appear in the previous site of some grain boundaries or directly on them. This supports the assumption that the stability of the grain boundaries is associated with the stability of the second phases and foreign materials accumulated on them, Fig.2.

The comparison[1,2] of the properties of samples heat treated directly or prepared from a heat treated wire indicates that the dislocation density is lower while the grain boundaries are cleaner in the samples heat treated after thinning. These observations prove that the samples for 100 kV TEM have to be considered as thin samples from the point of view of the diffusion and not representing the changes taking place within the doped bulk wire in all aspects. But we may state that recrystallisation can occur in thinned specimens, too. This being observed in the thinnest region, is supposed to be due to enhanced grain boundary diffusion of impurities or dopants to the surfaces /Fig.3./

At higher temperatures /1900 K/ the grain boundary movement stops possibly because of grain grooving[3].

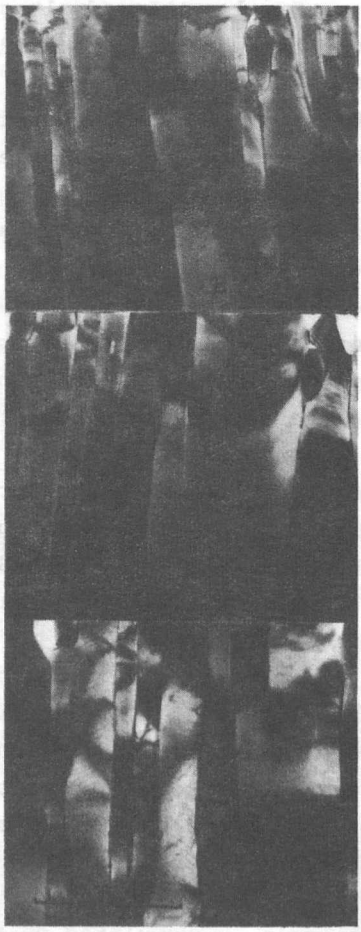

Fig.1. The same area after heat treatments for 30 s at 1300 K, 1500 K, 1700 K respectively. The development of a second phase /bubble/ row /A/ and the dissolution of a dislocation boundary /B/ can be observed.

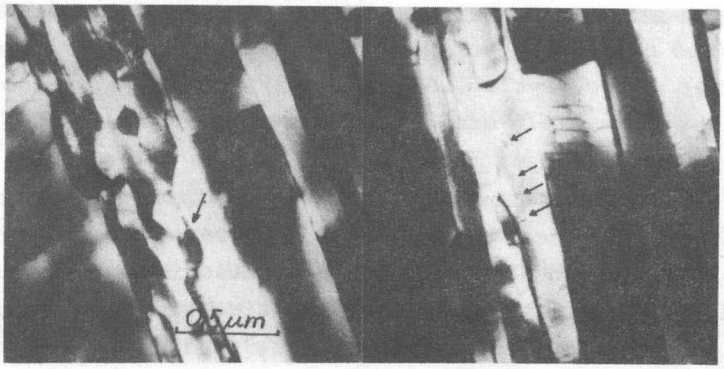

Fig.2. The same area at 1300 K and 1700 K. A bubble row formed on the spot of the grain boundary /arrowed/.

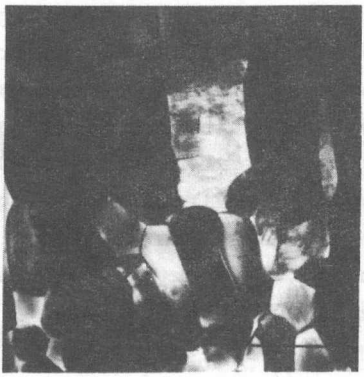

Fig.3. Recystallization in the thinnest region of the specimen after a heat treatment about 2500 K.

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LATTICE DEFECTS AND ELECTRICAL PROPERTIES OF Si DEVICES

E. Pál A. Vértesy[x]

The connection between electrical parameters of Si-based semiconductor devices and some of the characteristic lattice defects arising in Si during the technological process was studied. Test circuits containing transistors produced by planar technique on (111) Si wafers were studied by Lang, Berg--Barrett and double-crystal X-ray topography.

According to the topographs, near to the edges of the slices there are dislocation rows lying in the {111} slip planes inclined to the surface /Fig.1/. They may arise from the external deformations and the internal stresses during the high temperature processes. Crossing the active regions of the transistors these dislocations cause short-circuits or decreases in breakdown voltages between collector-emitter and collector--base junctions, as it was shown by electrical measurements [1].

A great number of slices produced by modified technology, i.e. by forcing the isolating boron-diffusion, was studied. Emitter-edge type dislocations of three different kinds arise from the boundary of the 8 /um wide, annulus-shaped boron--doped region within each chip /Fig.2./. They lie mostly in (111) planes parallel to the surface. Some of them lying relatively deeply, slip out to the surface in the {110} planes /Fig.3, arrow a/. Others are closing in a (111) plane like a half-loop to the boundary of the doped region mentioned above, as typical emitter-edge type dislocations /Fig.3, arrow b/. Dislocations of the third group start also like regular emitter-edge type dislocations, but they reach the surface before forming half-loop because they are lying in a (111) plane very near to the surface, and the surface is misoriented from (111) approximately by 3° /Fig.3, arrow c/.

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x Industrial Research Institute for Electronics /HIKI/

These emitter-edge type dislocations being present in the future emitter region can cause anomalous diffusion during the high concentration phosphorus emitter diffusion. Diffusion pipes and spikes can be formed along the dislocations when the active base region is thin enough /some tenths of /um/, significantly deteriorating the transistor characteristics /Fig.2/

Some of these samples were Au-doped on the back side. The emitter-edge type dislocations became electrically active because of the higher Au-concentration in their vicinity. This effect results in a further distortion of the breakdown characteristics and in a significant increase in leakage currents. Table I. shows the correlation between the leakage current of the emitter-base junction and the dislocation density as well as the mean dislocation length inside the emitter region.

Table I

E-B leakage current /uA	0.6	2	260	400	420
dislocation density line/cm^2	4000	5800	6000	8200	8000
main dislocation length /um	50	90	240	270	330

[1] E.K. Pál, A.J. Vértesy, F.G. Bereczkei: Acta Cryst. A34 Part S4, 279 /1978/

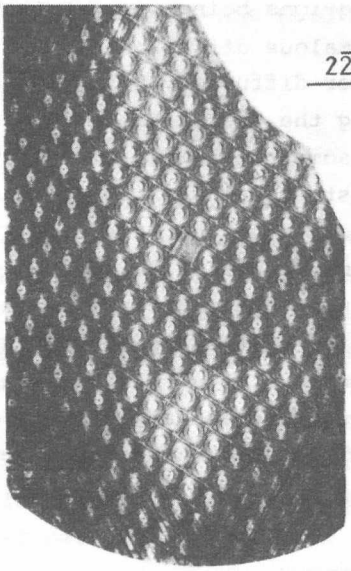


Fig.1

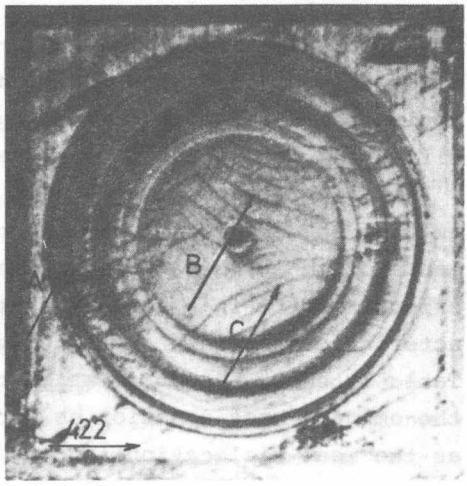


Fig.3

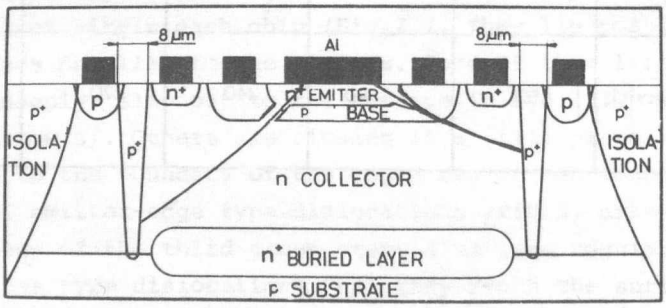


Fig.2: Formation of diffusion pipes and spikes along the dislocation lines

MASS SPECTROMETRIC STUDIES ON SOLID SURFACES

G. Gergely
I. Mojzes[+]
T. Sebestyen[+]
D. Szigethy

The evaporation of impurities and doping elements from solid surfaces was studied by a Riber QML51 quadrupole mass spectrometer. In this report ion emission of tungsten wires and the evaporation of As_2 or P_2 from contacted GaAs or GaP diodes resp. are briefly described. Tungsten wires used for incandescent lamp filaments are doped with K, Si and Al. Operating the filaments at high temperatures, the doping elements evaporate mainly in ionized form. The ion emission of tungsten wires especially the K^+ emission were studied in details earlier[1]. K^+ /T/ can be approximated by exponential terms

$$K^+ /T/ \sim A \exp\left(-E_i/kT\right)$$

with activation energy E_i. Below 2700 K $E_i \cong 4.8 - 5.8$ eV. Above this temperature E_i approximates 8 eV, and there the contribution of W^+ ions to the evaporation rate of tungsten becomes considerable.

The mass spectrometric study of As_2 and P_2 yields y/T/ during annealing of GaAs and GaP diodes resp. were followed by simultaneous recording of the diode resistance R/T/. Fig.1. represents typical results for a Gunn diode with AuGeNi contacts.

Abrupt rise of y/T/ occurs when the alloying temperature is reached. The latter is strongly affected by the composition and structure of the contact and substrate[2], as shown on Fig.2.

These studies supplied informations for the technology of Gunn diodes and enable to follow in situ the procedures of contacting[3].

[+] Semiconductor Research Division

Fig.1.

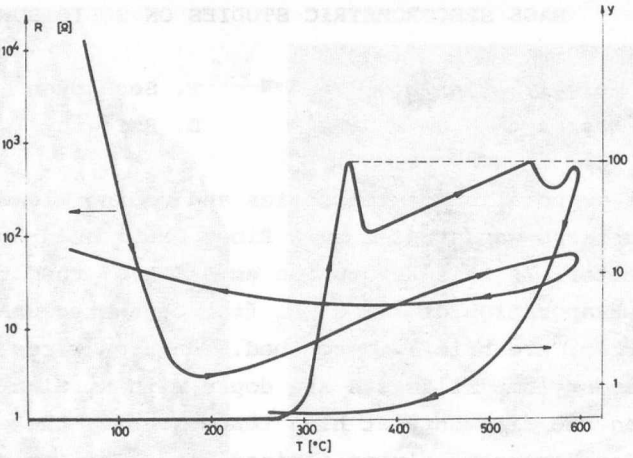
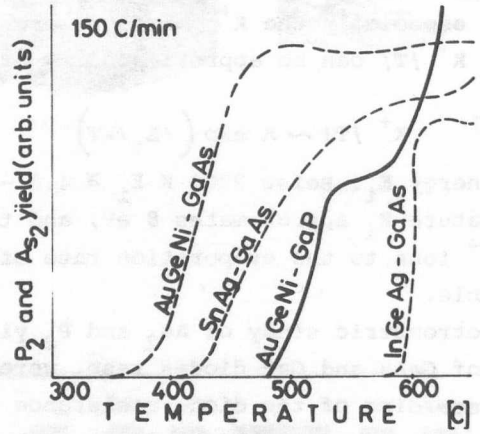


Fig.2.



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AUGER ELECTRON SPECTROSCOPIC STUDIES ON TUNGSTEN

G. Gergely M. Menyhárd

Auger electron spectroscopic studies were carried out on tungsten wires used in incandescent lamp technology. As-worked wires /doped by potassium aluminium silicate/ of 180 /um diameter were surface cleaned in ultra high vacuum and subjected to heat treatment to reduce the diffusion and the segregation of doping elements and impurities.

The surface composition of the wire is determined by the temperature and the number of cycles of heat treatment. The surface concentration of the single elements is, however, strongly affected by site competition. Further, the grain boundary diffusion has a dominant role in the fibrous unrecrystallized wire. Fig. 1. represents a typical Auger spectrum of segregated elements Si, S, P and C in carbide form[1].

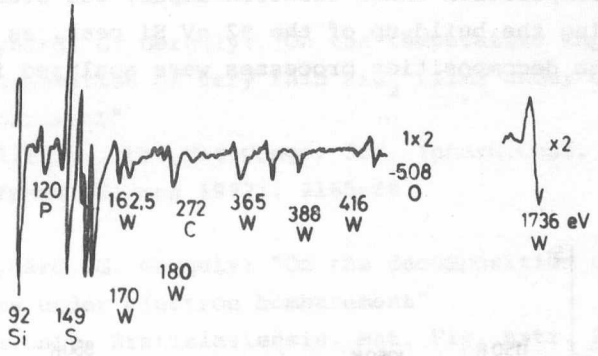

Fig.1.

Applying a suitable heat treatment process, some selected impurities can be revealed on the surface[2]. Fig.2. shows the changes in the sulphur concentration as a function of T on the surface. Fig.3. is its distribution along a wire sample.

AES proved to be suitable to detect trace amounts of S and to determine its spatial distribution on the wire surface[1,2].

The grain boundary diffusion of impurities, e.g. S, was studied by AES on tungsten wires[2].

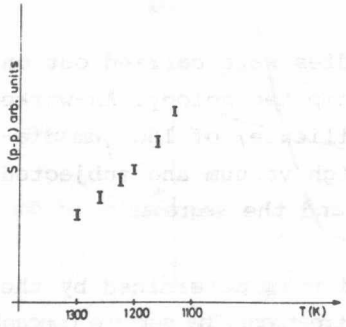

Fig.2.

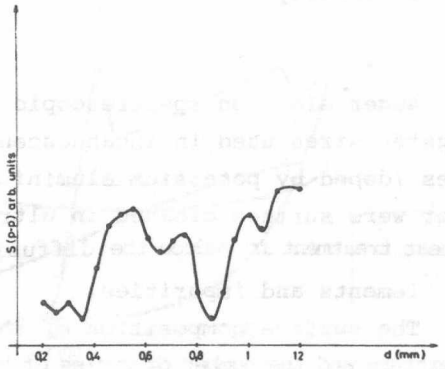

Fig.3

Using a suitable heat treatment process, it was possible to eliminate all segregating impurities but Si and O and to form a SiO_2 film of 1-2 monolayers on the wire surface.

Its decomposition under electron impact was studied by AES, detecting the build-up of the 92 eV Si peak, as presented on Fig.4. The decomposition processes were analysed in details[3,4].

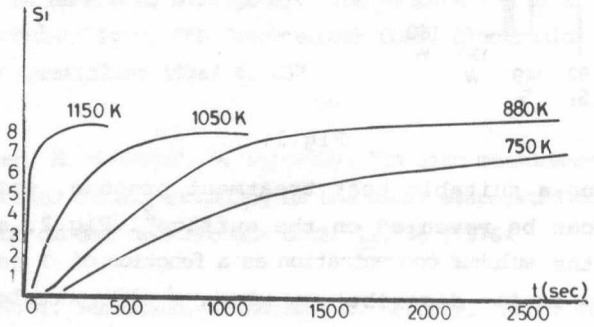

Fig.4.

Fracture surfaces of tungsten wires /subjected to various treatments/ were analysed by AES[5]. The fracturing path of "as--received" and recrystallized wires proved to be mainly determined by second phases of potassium. High bulk concentration of oxide second phases was identified as another reason of fracture.

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DIGITAL SIGNAL PROCESSING FOR QUANTITATIVE SEM

J.L.Lábár A.L. Tóth
I. Pozsgai A.E. Vladár

The SEM Laboratory of Structure Research Division serves to aid the basic and applied research of our Institute and our R+D cooperation for LSI circuit production. Digitalization provides natural extension of our previous qualitative measurements /failure analysis, qualitative X-ray and EBIC measurements/ on IC technology.

Our SEM has been equipped with a complex system to detect and exploit all of the available signals arising from the electron-solid interaction, Fig.1. To derive quantitative information from these data we extended our energy dispersive X-ray analyser /EDS/. As a first step the wavelength dispersive signal /WDS/ was collected in the multichannel analyser /MCA/.

Fig.2. illustrates the computer processing of a soft X-ray spectrum. The analysis of TiN is complicated due to the overlapping of N K_α and Ti Ll lines. By peak stripping the net N intensity can be obtained[1].

Any of the signals listed in Fig.1. can be digitalized and fed into the MCA memory using a voltage to frequency converter /VFC/, Fig.3. As a result, quantitative line scan measurements can be made for further computer processing. Complex mathematical and statistical data reduction is possible by this way.

Fig.4. demonstrates some of the signals detected by line scan across a LED specimen. The EBIC profil /showing the p-n junction/ is background-subtracted and plotted on log scale, too, for diffusion length measurements.[2]

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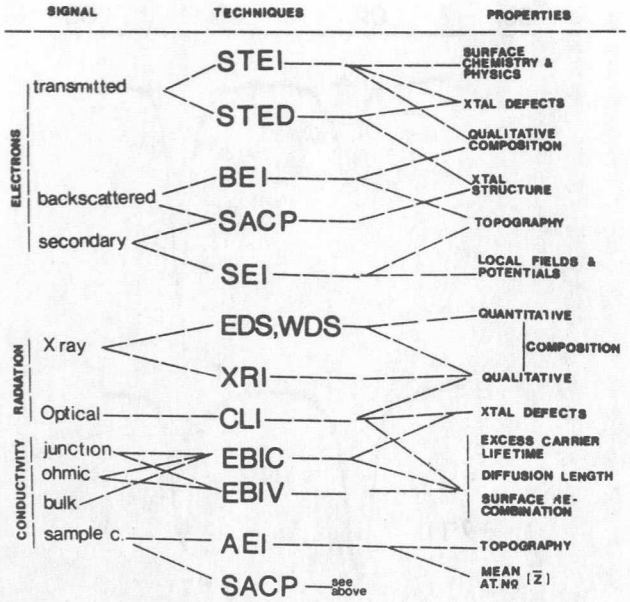

Fig.1. Signals and techniques used in SEM

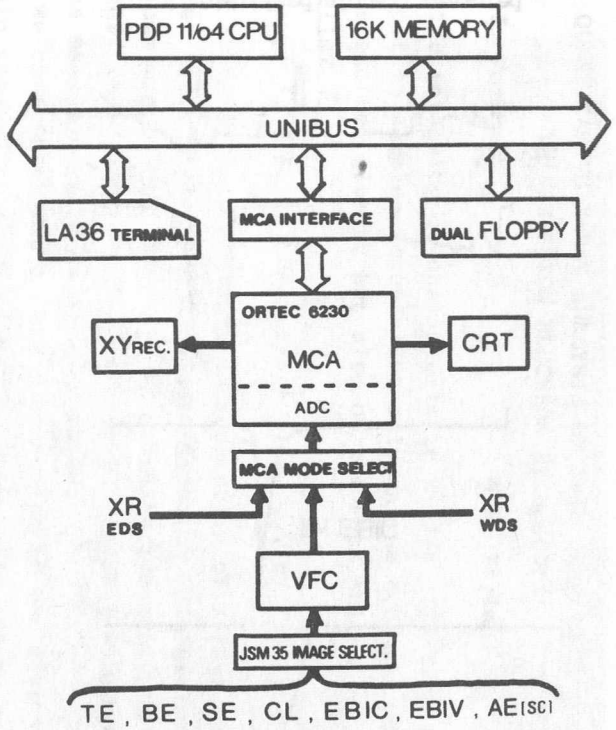

Fig.3. Digital processing of signals shown on Fig.1

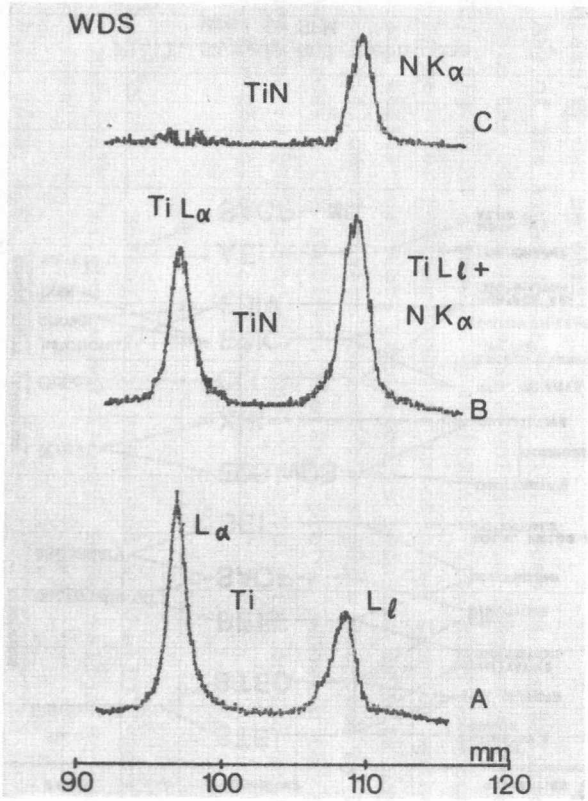

Fig.2. Peak stripping
$C = B - \alpha \cdot A$

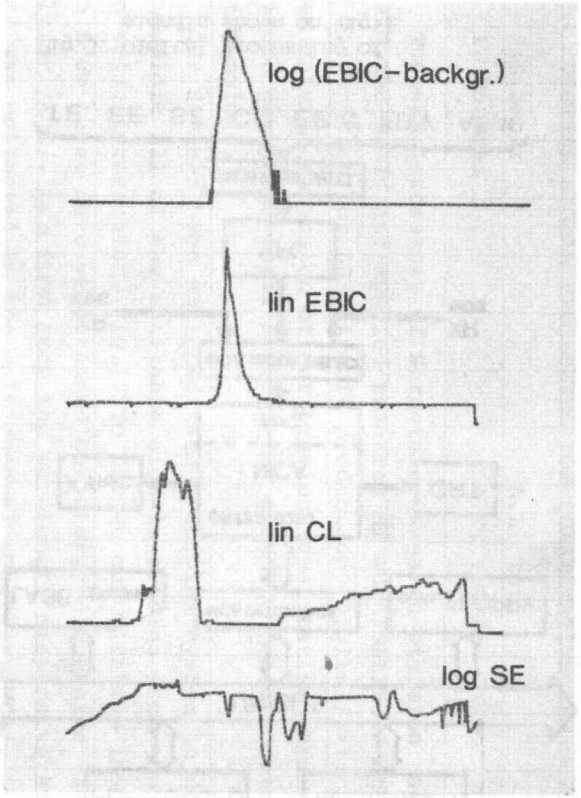

Fig.4. Digitized signals measured across a LED p-n junction

QUANTITATIVE X-RAY ANALYSIS OF THIN SAMPLES IN THE TRANSMISSION ELECTRON MICROSCOPE

I. Pozsgai N.P. Ilyin[+]

The intensity of characteristic X-rays /I_i^x/ from thin self-supporting samples depends not only on the concentration /c/ of the excited element but also on the mass thickness /ϱD/ of the film:

$$I_i^x = k_i \, c_i \, \varrho D f_i \qquad /i = 1, 2, \ldots n/ \qquad /1/$$

where f_i takes into account the absorption of X-rays in the sample. The k_i factors can be determined on thin etalon films of known thickness. To carry out quantitative analysis of thin samples, it is necessary to measure the local ϱD independently of the measurement of X-ray intensities.

We have developed a method to determine the mass thickness of thin samples by electron transmission[1] and their chemical composition by combining the X-ray intensity and electron transmission measurements[2]. For these studies we have used a transmission electron microscope of type JEOL 100 U equipped with a wavelenght dispersive X-ray spectrometer. The measured dependence of the contrast /$\lg \frac{I_o}{I_{tr}}$/ on ϱD can be expressed mathematically as follows:

$$\frac{\lg \left(I_o / I_{tr}\right) A}{7.64 \cdot 10^{-5} \, Z^{1.8}} = \varrho D \qquad /2/$$

where A, Z, I_o and I_{tr} are the atomic weight, the atomic number, the beam current and the integrated intensity of transmitted electrons. Eq.2. is valid at 100 kV for the given experimental set-up in the mass thickness range of 0.3 - 170 /ug/cm^2. Eq.2. can be generalized for multicomponent films[1] in the following form:

[+]Research Inst. for Geochemistry and Analytical Chemistry of the Soviet Academy of Sciences, Moscow

$$\frac{\lg\left(I_o/I_{tr}\right)}{7.64\cdot10^{-5}\ \sum_{i=1}^{n}\frac{c_i Z_i}{A_i}^{1.8}} = \varrho D \quad /i = 1, 2 \ldots n/ \qquad /3/$$

where c_i is the concentration of the i-th component. The ϱD of the sample to be analyzed as well as that of thin standards are measured according to Eq.3. The precision of the film thickness measurement is $\pm$ 3%, its reproducibility is better than $\pm$0,5%. Combining the measurement of X-ray intensities from the sample and thin standards with the measurement of ϱD according to Eq.3, ϱD and c_i can be separately determined. The deviation of the sum of concentrations from 100 % characterizes the accuracy of the analysis.

Table 1 shows the mass thickness and chemical composition of five FeNiMo films produced by sputtering from a single target material. The comparison of the average compositions of these films with the composition of the bulk target /analyzed with wet chemical methods/ is shown in Table 1, too.

Table 1

Sample	$D\left[\frac{/ug}{cm^2}\right]$	C_{Fe}%	C_{Ni}%	C_{Mo}%	$\sum c_i$
FeNiMo 200	19.9± 0.7	16.2 ±0.5	85.7 ± 0.3	3.4 ±0.1	105.3
FeNiMo 400	44.0± 0.2	16.3 ±0.08	80.5 ± 0.4	3.83±0.04	100.7
FeNiMo 600	64.7± 0.3	16.12±0.07	81.0 ± 0.3	3.53±0.01	100.6
FeNiMo 800	89.1± 2.5	16.2± 0.5	76.1 ± 2.2	3.5 ±0.1	95.8
FeNiMo 1000	114.9± 3.0	14.8± 0.4	78.4 ± 2.1	2.95±0.08	96.1
Average thin	-	15.9± 0.6	80.3 ± 3.5	3.5 ± 0.3	99.7
Bulk	-	17.0± 0.1	79.2 ± 0.2	3.4 ± 0.2	99.6

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ANALYTICAL DETERMINATION OF THE POTASSIUM CONTENT OF SINGLE BUBBLES IN ANNEALED TUNGSTEN WIRES

A.Barna J. Stark

It is well known that in severely drawn K-Al-Si doped tungsten wires rows of nearly equiaxial stress free second phases are formed during recrystallization.In thinned foils, at low temperatures, these second phases produce in many cases selected area diffraction patterns, suggesting the presence of crystalline potassium.

In the present work a TEM type JEOL 100 U supplied with a wavelength-dispersive X-ray spectrometer of type EM-AXA-5 was used.

By modifying the electron gun the spot size of the electron probe was reduced by an order of magnitude: the half width of the intensity distribution was less than 0.2 /um and the current density was less than 100 A/cm^2 at 100 kV. A magnetic field compensator in the vicinity of the optical column of the electron microscope eliminated the disturbing AC magnetic field of 3 to 6 mOe.

Figure 1.a.is a bright field image of a bubble in a tungsten matrix which is assumed to contain potassium. This assumption is based on the diffraction pattern shown in Fig. 1.b. that has some extra spots of small intensity. The dark field image in Fig.1·c.was taken by the beams belonging to the two weak extra reflections marked by a circle in Fig.1.b. According to the dark field image the two weak reflections in question come indeed from the bubble. The diffraction pattern of Fig.1.b. can be sufficiently interpreted by the assumption of the presence of potassium in the bubbles as shown in the indexing of Fig.1.d.

After focusing the electron beam onto a second phase, showing up in the selected area diffraction pattern as potassium /Fig.1/ the counts were measured.

The potassium standard was a 1 nm thick KCl film evaporated onto a 0.13 /um thick tungsten foil. The thickness of the foil was determined by means of the sample current . For the potassium K_{α} line of the standard, the peak-to-background ratio amounted to 1.45 at 100 kV. Allowing for the excited volume this signal corresponds to $2 \pm 0.5 \times 10^{-17}$ g potassium.

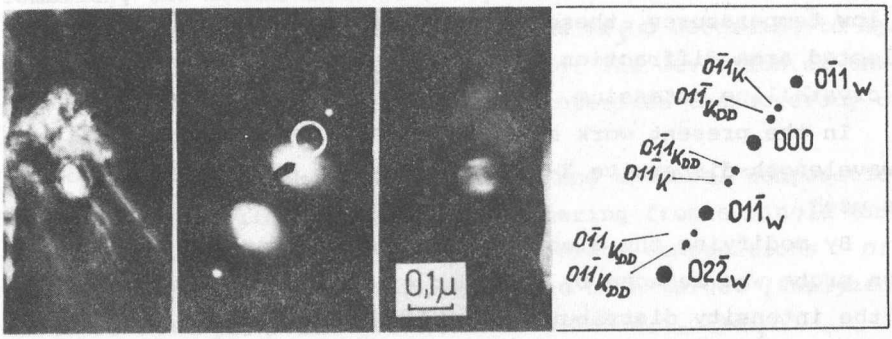

Fig.1. Second phase in a 0.173 /um thick tungsten wire annealed in dry hydrogen at 2800 K for 10 min. /a/ Bright field image, /b/ selected area diffraction pattern, /c/ dark field image taken by extra spots shown in /b/, /d/ indexing of diffraction pattern shown in /b/.

A. Barna, J. Stark: " Analytical determination of potassium content of simple bubbles in annealed tungsten wires" Metallurgical Transactions A 9 595-596 /1978/

DIVISION OF OPTICS AND ELECTRONICS

OUR WORK IN THE FIELD OF OPTICS AND ELECTRONICS

J. Schanda

Both optics and electronics become increasingly important in many areas of science and technology. This was early recognized by our Institute. Thus, some five years ago the Division of Optics and Electronics was established with the task to perform research in the field of light and optical radiation measurement, solid state optics and electronic data handling, partly in relation to the optical investigations but partly also serving the needs of the other departments of the Institute.

The Solid State Optics Department conducted investigations in the field of semiconductor research. Some of its activities were thoroughly coupled to the endeavours of the Semiconductor Research Division, and will be reviewed in the context of new results achieved there.

Some other work carried out by this group will be dealt with in this section of the yearbook: This will contain mainly information of more fundamental character /e.g. optical constants of Si /see p. 111 / and of layer structures grown onto Si substrates/ or dealing with new optical techniques /e.g. techniques of optical spectroscopy /see p. 116/ and of producing optical gratings/.

The Department of Photometry deals with many aspects of light and radiation measurement.

Due to the rapid development of electronic techniques in optics it became possible to establish the direct link between optical radiation and light measurement. Several aspects of these problems were dealt with in our Institute, starting with high precision radiation measurement and spectroradiometry[1], through goniometric measurements[2] to couple the unidirectional values with the generally used spherical ones, and ending up with some very special optical techniques used for the investigation of light emitting diode /LED/ characteristics[3] and non-visual effect of radiation[4].

A major endeavour of this department is to find more appropriate descriptions for the colorimetric characteristics of light sources. In this respect proposals were made for redefining the concept of correlated colour temperature[5] and colour rendering index in the light of the new CIE definitions for colour difference calculations /see also p. 121/.

A major joint effort of our Photometry and Electronics Departments is the development of advanced measuring methods of light and radiation. Characteristics of illuminance meters were investigated and techniques to evaluate these were developed[6]. The accurate measurements of colour and gloss were investigated and methods for modulating the spectral responsivity of detectors by filters to make them useful for colorimetric purposes /see p. 119/ as well as gloss-measuring instruments[7] were developed.

Instruments for the automatic goniometric measurement of lamps and luminaires[8] were also developed together with electronic equipments for the correct evaluation of nonsinusoidal current, voltage and power[2].

The Electronics Department dealt also with a number of further questions related to the activities of other sections of our Institute. These were partly basic problems of digital and analogue data handling, but a number of them were directly related to the investigations carried out in the other depart-

ments and are discussed in the respective sections of the Yearbook /see also p. 123/.

As the Division of Optics and Electronics of the Institute is the basic laboratory of the Academy in the field of light, colour and radiation measurement, it has the responsibility to cooperate in international organizations working in its line. As it is interested in the activities of basic radiometry and photometry its leader has been asked by the International Commission of Weights and Measures /CIPM/ to act as consultant in its Committee for Photometry and Colorimetry /CCPR/.

The world-wide activities in the field of illuminating engineering are coordinated by the International Commission on Illumination /CIE/, where we hold, for the time being, a chair in the Action Committee of this body, and also the Technical Committee on Photondetectors is chaired by our member. But coworkers of our Department of Photometry participate in the work of a number of other technical committees as well.

The colour work has its own international organization, the International Colour Association /AIC/, where one of the vice-presidents of the Association comes during this quadrennium from our Division. At the same time also one of the Technical Committees of the AIC is run by our Division.

The third aspect is measurement techniques. The international organization in this area is the International Measurement Technical Confederation /IMEKO/, where our Division is interested in its Technical Committee on Photondetectors, giving now the chairman of this committee.

These international relations enable the Division to act as mediator between the international and the national organizations, helping to keep pace with international achievements, assuring that the solutions they suggest to their Hungarian clients are always up-to-date.

1. G. Eppeldauer: "Electronics problems in optical measurements Lecture at the Conference on Optics '78, Budapest, Hungary 25-27 Sept. 1978.

2. G. Eppeldauer, K. Kántor, J.Schanda: "Automatic measurement of light distributions" Paper presented at the IMEKO Congress, Moscow, 21-27 May, 1979.

3. É.Pálmai, J.Schanda: "Measurements on optical displays" Lecture at the Conference on Electronic Components /Society for Telecommunications/, Kecskemét, Hungary, 10-12 Oct. 1978.

4. M. Urhegyi: "Measurement of biologically active optical radiation", Lecture at the Conference on Optics '78, Budapest, Hungary, 25-27 Sept. 1978.

5. J.Schanda, M.Mészáros, G. Czibula: "Calculating correlated color temperature with a desktop programable calculator" COLOR Res. and Appl. 3, 65 /1978/

6. G. Czibula, G. Dézsi, L. Szőnyi, J. Schanda: "On the determination of parameters of photodetectors used in illuminance meters" IMEKO Photondetector Symp., Praga, 21-24 Aug. 1978.

7. K. Kántor, K. Németh, "Gloss meter" Lectures at the Conference on Optics '78, Budapest 25-27 Sept. 1978. and at the XV. Symp. on Color, Héviz, 14-17 Nov. 1978.

8. G. Czibula, R. Brósz : "Light flux measurement of lamps with a goniophotometer" Lecture at the Conference on Optics '78, Budapest, 25-27 Sept. 1978.

OPTICAL CONSTANTS OF VARIOUS HEAVILY DOPED SILICON CRYSTALS OBTAINED BY A KRAMERS-KRONIG ANALYSIS

E.Barta

Optical testing of semiconductor device materials has become increasingly important being non-destructive and needing no contacts. The evaluation of the measurements requires, however, the knowledge of the wavelength and concentration dependence of the optical constants of the material. In restricted wavelength range a discrepancy between the theory and the available experimental data[1] led us to further investigation of this question.

The optical constants of heavily doped silicon were determined by a Kramers-Kronig analysis /KKA/. The optical constants thus obtained serve as a check of the experimental uncertainties[1] and of the theory as well.

As our experimental method and the adaptation of the KKA to the reflectivity curves of heavily doped silicon has been dealt with in two recent publications[2,3], here we shall only summarize the results and refer to these articles.

The adaptation of the KKA to variously doped Si-crystals led to the following results:

1. The index of refraction and extinction has been determined for the wavelength range 1-100 /um for various free carrier concentrations[3].

2. The concentration dependence of the absorption coefficient obtained from the KKA was in good agreement with the one expected from the semiclassical free carrier Drude model[3] indicating that the discrepancies found earlier[1] and leading to the conclusion that it may become necessary to alter the theory, may originate in experimental uncertainties due to the need for very thin samples, avoided in our work by analyzing reflectivity curves.

3. The effective mass could be calculated from the optical constants determined from the KKA thus avoiding the otherwise used approximations concerning the optical constants and/ /or the relaxation time /e.g. $n^2 \approx 1$, $k \approx 0$ at the reflectivity minimum, or $\omega^2 \tau^2 \approx 1$ etc./. It could be shown to which extent these approximations do not hold in the case of p- and n-type silicon and how this effects the value of the effective mass[2].

4. For the p-type samples it could be shown that the value of the optically determined effective mass is only in agreement with the one expected from theory if the contribution of the interband transitions to the dielectric constant was accounted for[2], as suggested by Lambert[4]. The correction regarding the interband transitions was carried out also for the effective mass values of Hara and Nishi[5] with the result that also in this case the discrepancy between their values and those expected from theory could be eliminated[2]. Thus our results provided an experimental verification of the calculations carried out by Lambert.

5. A relaxation time $\langle\tau\rangle_{KKA}$ could be obtained directly from the KKA results differing from $\langle\tau\rangle_{Hall}$ by a factor of 1.1 - 1.2 in the case of the samples investigated[3].

6. The KKA enabled a direct observation of the plasma-resonance frequency[2].

Our work has been carried out in the belief that recent progress in semiconductor technology in obtaining structures of given free carrier distributions and thus given optical behaviour will renew the interest in the question how free carriers influence the optical constants of semiconductor materials.

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3. E.Barta, F. Halász: "Optical constants of various heavily doped p- and n-type silicon crystals obtained by Kramer-Kronig analysis" Infrared Phys.17, 319 /1977/

4. L.M. Lambert: "Free carrier reflectivity in optically homogeneous silicon" Phys.Stat.Sol./2/,11, 461 /1972/

5. H.Hara, Y.Nishi:"Free carrier absorption in p-type silicon" J.Phys.Soc.Jap. 21, 1222 /1966/

INFRARED ABSORPTION OF DIELECTRIC FILMS ON SILICON SURFACE

G. Hoffmann

Infrared IR absorption measurements can give a better insight into the structure and composition of dielectric films on Si substrates.

A SiO_2 film grown on Si is usually not homogeneous, but a characteristic distribution of OH-groups can be found across the layer[1]. The treatment of these SiO_2 layers on silicon slices with diethyl ether vapour results in a diminished hydrogen content and a rearranged structure. Electrical measurements have revealed an increase in the breakdown strength and measurements of infrared absorption have shown a displacement and a decrease of the characteristic ν/Si-O/ = 1100 cm^{-1} and ν/OH/ = 3000-4000 cm^{-1} multiple internal reflection /MIR/ peaks. This substantiates the view that diethyl ether induces compositional and structural changes in SiO_2. We discuss the possible ways in which hydroxyl radicals are removed and we emphasize the roles of unshared electron pairs and of hydrogen bonding.

Doped oxides are used in semiconductor technology as diffusion sources. The phosphorus concentrations of p-doped SiO_2 films deposited onto Si wafers by pyrolysis have been determined by activation analysis and using the data of the diffusion layer prepared by the doped SiO_2 film in the Si substrate[2]. Using these P concentrations and the P-O IR absorption band of the films the constant K′ of the IR P determination has been calculated. Inversely, measuring the IR absorption band corresponding to the P-O groups and knowing the constant K′, one can give estimates of the surface concentration of the diffusion layer prepared by the SiO_2 diffusion source and of the p-n junction depth. The values of the constant K′ for SiO_2 film doped by triethylphosphate and

$POCl_3$ are significantly different. This can be explained by the difference in the ratio of the concentration of P-O bonds to the concentration of P atoms for the two doping materials.

Si_3N_4 films deposited onto Si substrates contain NH and SiH groups[3]. The effects of high temperature annealing on the structural and electrical properties of MNOS memory structures have been studied using MIR spectroscopy to determine the N-H and Si-H bonds in Si_3N_4 layer. Electrical methods applied were: the memory window decay rate, analysis of memory hysteresis, C-V curves and TSC technique. Results showed that there is an important role of the annealing temperature in the change of number of N-H and Si-H bonds in the vicinity of SiO_2-Si_3N_4 interface. The change of fixed charge at the SiO_2-Si_3N_4 interface, the retention time and width of memory window are closely related to the change in the number of the Si-H and N-H groups. Electrical data showed a strong dependence not only on annealing temperature and time but also on the composition of gas atmosphere used during annealing. The TSC curves were significantly different for the annealed and unannealed MNOS structures.

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2. G. Hoffmann, L. Puskás, M. Lőrinczy and A. Nagy: J. Phys. D: Appl. Phys. 12, 569-577 /1979/

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OPTICAL INVESTIGATIONS OF III-V COMPOUNDS

M.Gál

Practical semiconductor materials contain impurities and defects. Detailed information about these centres is of vital importance to semiconductor technologists and device engineers.

We have been using photoluminescence measurement techniques in order to characterize the impurities found in the III-V type materials grown in our Institute. In addition to the conventional photoluminescence technique, we have been using the temperature modulated photoluminescence /TMP/ method to obtain further information on the thermal effects influencing radiative recombination[1]. Since the TMP signal is proportional to the temperature derivative of the luminescence intensity, hidden structures in the emission spectra can be enhanced and closely lying emission lines can be separated [2]. /Fig.1/

We have measured the TMP spectra of excitons bound to isolated nitrogen and to nitrogen pairs in GaP. Our results indicate that second-order resonant transitions of the bound excitons play an important role in the radiative recombination[3]. In samples doped heavily with nitrogen, we have found evidence of temperature dependent tunnelling of excitons between the nitrogen atoms[3].

1. M. Gál: Phys. Rev.-B. 18, 803 /1978/

2. M. Gál: J. of Lumineschence, 17, 359 /1978/

3. M. Gál: Int. Conf. of Luminescence, Paris 1978.

PREPARATION OF OPTICAL GRATINGS ON THE SURFACE OF SEMICONDUCTORS

L. Andor

In producing integrated optical elements one of the first problems to be solved is the coupling of light into or out of an optical waveguide. For these experiments gratings couplers and reflectors were developed. Different methods gave us 1 /um and 0.35 /um gratings on GaAs, SiO_2, Si and Al layers.The following methods were used:

a/ Photochemical etching

The periodic intensity distribution of coherent light in the plane of the object affects the chemical etching rate periodically. This technique was used to produce gratings on GaAs-type materials /grating constants were 0.35 /um and 1 /um/.

b/ Photolithographic chemical etching

The interference picture produces a periodic structure in the photoresist, which is then etched into the waveguide material. In this case the chemical etching process limits the usable layer materials. We made 1 /um grating on SiO_2 with this method.

c/ Photolithographic ion milling

The periodic photoresist structure is transferred to the appropriate material by Argon ion milling. This method has the advantage of the ion milling process, so any layer material can be used[x]. In this case we could also make gratings with asymmetric profile /on GaAs: 0.35 /um sawteeth shaped gratings were produced/.

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[x] The ion milling is made in cooperation with the Central Research Institute for Physics of the Hungarian Academy of Sciences.

AUTOMATIC MEASUREMENT OF LIGHT DISTRIBUTIONS

R. Brósz G. Czibula
G. Eppeldauer K. Kántor

The investigation of light distributions of light sources and luminaires is important for both the quality control and the improvement of manufacturing design and technology.

This goniometric measurement requires the acquisition and handling of many thousands of data to give the proper curves and tables for lighting engineers.

We developed in our Institute two gonio-photometers, one for the light flux measurement of lamps, the other for investigating the light distribution indicatrix of luminaires.

The first instrument[1] is directly coupled to a minicomputer regulating the rotation of the goniometer and handling the measured data.

For investigating luminairs a two-axis goniometer was built[2] for an industrial laboratory. A secondary light detector serves to monitor the light of the luminaire at a fixed position compared to the source and correcting for all variations of light output during the measurement.

The realized control and measuring system of this instrument uses a multipurpose hybrid arithmetic unit and measures not only the electrical RMS characteristics of lamps to be examined but also the different /normalized/ photometric quantities.

1. G. Czibula, R. Brósz: Conference on Optics '78 Budapest.
2. G. Eppeldauer, K. Kántor, J. Schanda: Paper presented at the IMEKO Congress, Moscow, 21-27 May, 1979.

MEASUREMENT OF LIGHT, COLOUR AND BIOLOGICALLY ACTIVE RADIATION

G. Czibula S. Ferenczi
M. Vanyek-Urhegyi

For optical measurements in the practice the characteristics of photodetectors have to be known to be able to perform meaningful measurements[1]. The spectral responsivity has to be measured[2] and the correction of this spectral responsivity to that of some prescribed functions has to be performed. It is usual to perform this spectral adjustment by putting colour correcting filters in front of the detectors. The problem is to optimize the filter thicknesses and this is done in our Institute by using the following equation[3].

$$\tau(\lambda) = A \prod_{j=1}^{n} \tau_i^{h_i/h_{io}}$$

where $\tau(\lambda)$ = the spectral transmittance
A = the interreflection constant
$\tau_i(\lambda, h_{io})$ = the spectral transmittance of the filter with a thickness of h_{io}
h_i = the thickness of the filter.

The coupled responsivity of the filter and detector system is

$$s(\lambda) = s_o(\lambda) \cdot \tau(\lambda)$$

where $s_o(\lambda)$ - is the responsivity of the detector.

The first step is to choose the appropriate filters and then to optimize the filter thicknesses by using an iteration technique. Our program computes the following equation:

$$F(h_1, h_2 \ldots h_n) = \int_{\lambda_1}^{\lambda_2} \left[\frac{C(\lambda)}{\int_{\lambda_1}^{\lambda_2} \tau(\lambda) d\lambda} - \frac{s(\lambda)}{\int_{\lambda_1}^{\lambda_2} s(\lambda) d\lambda} \right] d\lambda = \min$$

where $F/h_1, h_2 \ldots h_n/$ = the function to be minimized
$C(\lambda)$ = the responsivity to be achieved
λ_1, λ_2 = the lower and higher ends of the spectral range.

Similar techniques - partially coupled with luminescent wavelength converters - can be used to correct the detector responsivity to the desired form in the ultraviolet.

The problem of amplifying the photodetector signal has also been solved. Thus, we were able to build stable and highly sensitive instruments for the different tasks mentioned above. We would like to mention only three instruments of this line: an illuminance meter with a responsivity as high as 10 mlx; a colorimeter specially designed for the measurement of colour television display tubes, where the operator has to push a single button to perform the measurement, and the luminance of the picture tube as well as the chromaticity coordinates are directly displayed, and a combined radiometer measuring UV A, B, C radiation, light, as well as infrared A and B radiation[4].

1. J. Schanda: 5th International Conference on Photoelectrical and Optical Properties, Varna, May 9-12, 1977

2. G. Eppeldauer, J. Gráner, J. Schanda, M. Vanyek-Urhegyi: Appl. Optics, 16, 255 /1977/

3. G. Czibula: XV. Symp. on Color, Héviz, Hungary, 14-17 Nov. 1978.

4. M. Urhegyi: Conference on Optics '78, Budapest, 25-27 Sept. 1978.

THE IMPORTANCE OF THE COLOUR RENDERING INDEX IN ILLUMINATING ENGINEERING

J. Schanda

The spectral power distribution of modern light sources can be tailored at will. The efficiency of light generations - lamp efficacy - is not the only parameter guiding lamp manufacturers in developing new lamp types.

The next most important lamp characteristic is colour rendering, the ability of the lamp to render colours in a "natural" way, i.e. so as seen under natural sources, daylight or incandescent light.

In recent years several lamp companies introduced their three band fluorescent lamps[1,2], where they tried to optimize both efficacy and colour rendering.

Several starting points of colour rendering calculations date back to early developments of fluorescent lamps, and are not necessarily valid today:

1. Correlated colour temperature and colour differences are calculated using the CIE 1964 UVW space, surpassed now with the two new recommendations of 1976.

2. CIE test samples were selected having only continuous sources in mind. For new line sources and new colour spaces these test surfaces seem to be not optimal. They do not sample colour space evenly enough.

3. Colour rendering itself is not the most important colorimetric attribute of a light source. Appreciative vision is better described by colour preference, where a number of further questions have to be solved. The most important of these is the selection of target chromaticities.

In recent papers we discussed the problem of redefining the concept of correlated colour temperature[3,4], and showed what changes might be introduced by adopting the CIELAB space

for colour rendering calculations[5], and suggested a combined colour rendering- colour preference index[6].

It is hoped that along these lines a new method of colour rendition can be established by the help of which a lamp construction technology can be established leading to the development of light sources with markedly better characteristics.

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4. J.Schanda: "Correlated colour temperature and the E^{x}_{ab} colour difference formula" 3rd Congress AIC COLOR 77, Troy,N.Y.July 10-15, 1977.

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6. J.Schanda: "Colour rendering and the impression of comfort with artificial illumination" Information Couleur, 3, 23-28 /1978/

NEW ELECTRONIC INSTRUMENT DEVELOPMENTS

G.Eppeldauer

The Electronic Department of the Institute deals with special custom-made instrumentation problems raised by the research groups of the Institute. Our group developed in the last years light and colour measuring equipments, regulated electric supplies, interface and display units, as well as temperature measuring instruments. Technical parameters of some of these instruments are as follows:

Combined illuminance and irradiance meter

The instrument measures the illuminance and the UV and IR irradiance with thermostated special measuring heads. It can be used to measure illuminance ratios, intensity of actinic radiations. The ranges are: 19.99, 199.9, 1999, 19990 lux.

LED measuring instrument

The instrument measures the light intensity, luminous flux and number of emitted quanta of green, yellow and red LED's. Measuring ranges are:

luminous flux	0 - 199.9 mlumen
light intensity	0 - 199.9 mCd
photon numbers	10^{13} ... 10^{16} n/s

Gloss-meter

It measures the gloss of enamels, paints and lacquers. Two measuring heads enable the measuring geometry of 20^{o} or 45^{o} and 85^{o}. Ratio measuring mode increases selectivity on diffuse surfaces.

Adaptor to light distribution measuring arrangements

It is suitable for RMS current, voltage and power measurements of light sources. It can also be used for measuring illuminance ratios for eliminating fluctuation of the light intensity of unstable sources.

Accuracy in RMS value measurements: $\pm$ 0.2 %

Resolution in illuminance meas.mode: 10^{-3} lux

Digital ratiometer-panelmeter

Short circuit current input or voltage input for both the numerator and denominator. Rated denominator range is 1 decade. 3 1/2 digit display, BCD output. Accuracy: ± 0.1 %. System compatibility.

Automatic TV tube colorimeter

The luminance and the chromaticity coordinates can be measured automatically. The resolution is 0.1 Cd/m^2. The accuracy is 0.05 unit. Measuring time: max. 10 s.

300 V, 6 A regulated power supply

The instrument works in constant current and constant voltage operation mode. The stability is better than 0.1 %.

Xenon lamps supply and spectroscopic arc source

The high voltage r.f. ignition and d.c. regulated current supply is used to feed arcs and lamps.

Nominal lamp power is 450 or 950 W
Stability is better than ± 0.3 %

Matrix display

The light emitting diode matrix arrangement can display 9 different levels of max. 16 signals in form of discrete or continuous curves instead of using an oscilloscope.

Display and tape punch interface

Digitally coded results and symbols can be displayed and interfaced to data registers or computers in standard ASC II. code.

Digital thermometer

This precision temperature measuring device can be used with a Pt-PtRh thermoelement and is linearized for the temperature range 0 - 1599.9°C. Cold junction compensation is applied.

Linearity: ± 2°C
Stability: 0.5°C/month

85.1 XII. 11.