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INTRODUCTION TO THE COLLECTION ON MATERIAL SCIENCE

Material research and engineering have recently gained very high significance. The industry is looking for new materials mainly laying stress on the ecological point of view as well as on economical aspects. The material boom has mainly appeared within electronic, optoelectronic and optical devices. Researchers are studying possibilities of minimizing the size of final products and of decreasing energy for their preparation. On the other hand such a search is limited by the ecological boundaries in order to obtain materials enabling their recycling preferably without giving rise to a harmful waste products.

We would like to focus our attention on the field of semiconductors respecting our Institute of Physics in Prague where the semiconductor research has gained a definite international respect. It had a world priority in inventing the first transistor upon the well-managed preparation of silicon single crystal using a unique flow-zone melting. In the fifties, the communist regime, however, did not see any way of applying the transistor and did not give any chance of its further developing. Not less important were the research achievements in amorphous chalcogenide semiconductors based on a well-understood technology of rapid cooling of melts developed in the seventies. Nevertheless, the gap between the fast progress in western semiconductor technology and that the east, where we belonged until 1990, widened, and led to the desolate state of communist electronics. After starting the restructuralization started in 1991, an undesired effect resulted in the separation of physics instead in the expected integration of all specializations attempting to diminish the number of technologists craftsmen in many institute lacking consequently specialists for west technology transfers.

Generally in basic material research, we focus on the structure, properties, phenomena, or behaviour of materials. The functional utility of a new material, however, need not be appreciated until its properties are adequately characterized. As an example may serve quasi-crystals, a class of materials neither exactly crystalline nor amorphous, but with some attributes of both. These materials were discovered only in this decade. Properties of this class of materials are still being measured, and it is not clear which functional property will result in an application.

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Properties are the indicators that define the functional attributes and utility of materials. The brilliance and transparency of diamond, for example, give rise to its use as a gemstone, as well as sophisticated optical coatings, while its great hardness and thermal conductivity permit quite different applications, such as cutting tools and media.

Property measurements and their analysis are the domains of theoretical and experimental physicists, physical chemists, metallurgists, chemists, polymer chemists and engineers of all fields. Characterization of some properties on an atomic scale is a research area in the forefront of theoretical physics–theories of phase transitions in magnetic materials and in ferroelectrics are cases in point. Similarly, elucidation of the fracture mechanics of brittle ceramists and metallic materials is a focus of research by metallurgists, ceramic and solid-state physicists. The understanding of properties and structure in tandem has enabled synthetic chemists to make materials with 'better', or at least predictably different, 'taylorable', properties. This interrelationship affects the ultimate utility of materials – their performance. Two of Nobel Prizes were awarded for the discovery of the quantum Hall effect and for the work on high-T_c superconductivity in research based on innovative property determinations. The latter, of course, was also a triumph of synthesis and analysis.

New emphasis in material science and engineering was put on the nanometer and two-dimensional size regime, which is intermediate between the well-studied macroscopic and atomic levels. This regime is pivotal in the understanding the magnetic, electronic and optical properties of materials. Knowledge of structural and compositional features in the nanometer size of so called 'medium range ordering' is also important for interfaces between dissimilar materials, such as those that occur in composite structural materials or in complex multimaterial devices that make up integrated electronic circuitry.

The development of new materials and of material systems structured on an atomic scale is a recent phenomenon that will have many important applications. For example, the processes used for producing artificially structured materials make it possible to combine optically active materials with electronic circuitry in a way that should lead to qualitatively new kinds of optoelectronic devices. Artificially structured materials can be produced by variety of new techniques, including chemical beam epitaxy (CBE), metal-organic molecular beam epitaxy (MOMBE), and low-pressure chemical vapor deposition (LPCVD).

Vapor-solid processing is becoming an increasingly important tool for achieving ultrafine structures, epitaxial layers, surface coatings, and bulk forms in single shapes. The list of processes used is very long and includes physical vapor deposition, CVD, plasma-assisted vapor deposition, metal-organic chemical vapor deposition, MBE, and ion beam deposition. Vapor deposition processes are used extensively in the electronic material industry to build chip structures.

Microelectronics is entering the submicron feature regime in which new classes of physical phenomena and materials structures determine device behavior. Materials demands can only be expected to increase but material development cannot be isolated from the processing research and device design.

Foreseeable changes in silicon technology will include flatter wafers, lower defect density (less than one defect per wafer), larger wafer diameter, and smaller feature size. To reliably achieve submicron circuit features, improved photolithographic processes will be needed. A combination of advanced optical methods (excimer lasers) and new materials (ultraviolet-activated photoresists and multilevel resists), will be used to produce features down to 0.3 to 0.5 μm.

Although silicon will dominate the electronics community in the foreseeable future, much research effort is being devoted to the development of III–V semiconductor compounds, such as gallium arsenide (GaAs) for specific applications, Because of their electronic structures, their high electron mobilities, and the manner in which excited electrons in III–V compounds lose their energy by emitting light, III–V materials provide higher-frequency capabilities than silicon does and they are optically active, being both laser sources and detectors.

In the growth of gallium arsenide (GaAs) and indium phosphide (InP), the primary needs are improved crystal purity, perfection and size. An emerging technology that seems almost certain to become important is the epitaxial growth of GaAs on silicon and extensions involving optical detector regions (e.g., mercury–cadmium–telluride for infrared). A critical issue for the formation of a GaAs/InP industry will be the ability to transfer epitaxial growth processes from the laboratory to a manufacturing facility.

Thermodynamics, however, has occupied the first position in the processes of new material preparation and in the forecast of their physical-chemical behavior. There is probably no other broad subject that impinges more on the various aspects of materials science and engineering than the description of face stability in terms of temperature, composition, pressure, etc. The resulting 'road maps' called phase diagrams guide and direct us to numerous goals in fabrication, heat treatment, alloy design and any further basic understanding of 'real' materials in their frequent phase metastability/instability.

Nucleation and growth processes have been important areas of research for more than 30 years. Today, important research topics on nucleation deal with the question of how to avoid it to achieve high undercoolings and, hence, nonequlibrium structures in materials and how to promote it to achieve fine grain sizes. Topics in growth deal with interfacial phenomena, dendritic growth mechanisms, nonequlibrium processes and formation of heterogeneities such as lattice defects, segregation, porosity, and inclusions.

Thermodynamic considerations of chemical processing serve the technologists as a very useful method already asserted in the preparation of the first electronic material–silicon. There were many problems to be overcome, such as the oxidation of silicon during its preparation and then during its crystal growth. The evaluation of the phase diagrams made it possible to solve this

problem and to draw up the method of the preparation of single crystals of silicon without oxides. Then the thermodynamics solved successfully the doping of silicon with various elements and so enabled the production of cheap the silicon single crystals with *p*- and *n*-type of conductivity. However, in the case of the silicon growth only a binary system has been solved but advanced thermodynamics also showed its quality in the preparation of multicomponent compounds based on indium antimonide, indium phosphide, boron nitride, or aluminium nitride.

In recent years, great advances have been made in growing single crystals; a notable example is provided by the semiconductor industry, in which, during the last 20 years, the size of silicon single crystals grown from the melt has increased from 1 in. (2.5 cm) in diameter to more than 6 in. (15 cm) in diameter (with further increases expected in the future), while the dislocation content of these crystals has dropped from 100 to 1000 cm^{-2} to practically zero.

It is worth noting that the thermodynamics played a significant role in the preparation of semiconducting gallium arsenide which has a high tendency to oxidize. Therefore the single crystals were prepared in the evacuated quartz ampoule, but it was found that at the very high (1511 K) melting point of GaAs oxygen is released from SiO_2. Thus, the prepared GaAs always contained a small amount of gallium oxide and silicon which as impurities in single crystals. Therefore it was possible to prepare neither undoped GaAs nor semiinsulating GaAs. Single crystals were effectively doped by silicon in the concentration of about 1×10^{-18} atoms·cm^{-3} and the crystal surface was polluted by polycrystalline scum which was identified as gallium oxide and silicon oxide. The technologists made use of other materials for the growth devices such as pyrolytic boron nitride which again provided a small concentration of boron in the final crystals. It is true, however, that the boron concentration was lower than in the case of silicon but single crystals contained always undesirable elements from the sample holder.

The optimal solution was not found until the thermodynamic analysis was applied. A small amount of gallium oxide was added in the starting polycrystalline GaAs material by which the resolution of quartz was suppressed. After this success of thermodynamic calculation, the thermodynamic methods came successfully into the technology of single crystal growth because it threw new light on the behavior of low concentration in the multicomponent compounds and thus helped in their preparation. So the thermodynamics becomes attractive for the technologists preparing the III–V, IV–VI and II–VI semiconductor compounds which are used so far in the fabrication of optoelectronic and electronic devices.

Not less important is the use of the thermodynamics in the growth of ternary or quaternary or muticomponent compounds prepared by using various technological methods. For example, the thermodynamics solved the growth problems in the case of the preparation of IV–VI optoelectronic and electronic materials

grown by means of vapor methods, such as germanium sulphides and germanium selenides.

At the Institute of Physics in Prague thermodynamic evaluations are applied to assist the preparation of special single crystals needed for physical measurements and applications. It is necessary to notice that this evaluation of the crystal conditions is also effective for a very low concentration of dopants, i.e. in the range of 1×10^{16}–1×10^{19} atoms·cm^{-3} which is 0.01–0.00001% dopant in the starting material. For example, the way how to prepare gallium antimonide (GaSb) doped by sulphur in the concentration of 1×10^{16}–1×10^{17} atoms·cm^{-3} was described. Additionally, it was possible to explain the double doping of tellurium and sulphur in GaSb single crystals and finally to prepare these crystals with various concentrations of both elements.

The facts mentioned above show that the thermodynamic studies are very important to improve the crystal growth technology and are able to assist to solve complicated technological procedures. Similarly a thermodynamic calculation is applied in the case of the preparation of thin layers when, on the one hand, the concentration of the components are low and, on the other hand, the total amount of the final compound represents only several micrograms. It is hoped that the so-called micro-phase diagrams will show where one component will be in the extremely low concentration down to about 0.001–0.0000001%. Finally, as materials become purer and more microscopically controlled, the requirements for materials characterization become even more stringent. Monitoring the amount, identity, and location of each chemical or even each atomic constituent in situ in real time, and often during the fabrication process itself, will require substantial research into characterization.

The recent shift from electronic to optical technology has required the development, production, and fabrication of many new materials. The development of new process technology resulted in silica optical fibers with transmission losses approaching the theoretical minimum. For optical emitters and detectors, III–V semiconductors are the materials of choice. Indium phosphide substrates with gallium-indium-arsenide-phosphide epitaxial layers are used to generate radiation at 1.3 and 1.5 μm as input to optical fibers.

As basic knowledge of surfaces and epitaxial layer formation has evolved, new emphasis has been put to heteroepitaxy of one material on another to achieve novel devices or to use the best features of each layer. For example, GaAs is being grown on silicon for integrated optics in which laser or detector devices are directly associated with silicon circuitry. Vertically integrated structures containing epitaxial insulators and metals are also being studied – for example, calcium fluoride or cobalt silicide on silicon. Growth processes are difficult to control for these materials, requiring the development of new high-resolution techniques for interface studies.

Modern materials engineering involves exploitation of relationships among the basic elements of the field: structure and state composition and properties, synthesis and processing, and performance and industrial as well as broader

societal needs. Some important materials discoveries have been made by scientists, some by engineers, and still others by craftsmen. Many have been made by teams comprising all three types of individuals, thermal treatment and analysis being the integrating feature.

Thermal analysis does not play a marginal role in the new material investigation. It is a natural part of all high and/or low temperature measurements recently showing, e.g., its irreplaceable value in search for new high temperature oxide superconductors. Many articles appeared in various material research journals recognizing thermal analysis as a part of convenient thermophysical measurements. It was equally reflected in the foundation of conference sections on material science and engineering at various meetings dealing with thermal analysis, calorimetry and thermodynamics in general. It was, for example, the 10th ICTA in Hatfield (1992), the 28th Jpn. Conference on Thermal Analysis and Calorimetry in Tokyo (1992) or the 5th ESTAC in Grado (1994) and 49th Calorimetry U.S. Conference in Santa Fe (1994). In relation to this trend the working group on advanced inorganic materials was created within the ICTAC framework needed by J. Sesták who also recently edited a 700 pp book entitled 'Special Technologies and Materials' (published in Czech Academia, Prague 1993). The tradition of material science sections was also maintained during the Czechoslovak–French–Polish Conference on Calorimetry and Experimental Thermodynamics held in Prague, September 1993. This special issue of Journal Thermal Analysis is a collection of the papers presented there within material section moderated by the editors who hope it will be accepted as a confirmation of the successful series presenting this interdisciplinary art of applied science to our thermoanalytical family.

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