NATIONAL BUREAU OF STANDARDS REPORT

9591

RESEARCH ON CRYSTAL GROWTH AND CHARACTERIZATION

AND HIGH TEMPERATURE AND LASER MATERIALS

Edited by

Elio Passaglia

Period Covered

January 1, 1967 - July 1, 1967

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

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Research on Crystal Growth and Characterization and High Temperature and Laser Materials At The National Bureau of Standards

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1. INTRODUCTION

Before July 1, 1966 this program was concerned solely with crystal growth and characterization. Beginning with that date, the emphasis was changed to include high temperature and laser materials. Previous semiannual reports in this series were published as NBS Technical Notes, "Research on Crystal Growth and Characterization at the National Bureau of Standards", but with this shift of emphasis this report is published as a Report to the Sponsor.

This report is divided into two sections: Crystal Growth and Characterization, and High Temperature and Laser Materials. Subsequent reports will not include the section on Crystal Growth and Characterization.

2. CRYSTAL GROWTH AND CHARACTERIZATION

2.1 Interface Kinetics of Growth of Metal Crystals from the Melt

J. G. Early and H. P. Utech

Crystallization of Metals Section

Our early experiments on the crystallization kinetics of Sn emphasized the importance of using a crucible of very low thermal conductivity. This has led us to use crucibles of poly (tetrafluoroethylene) (PTFE) backed by stainless steel. This effectively solved the short-circuiting problem, and we are currently investigating whether the PTFE is introducing impurities into the tin melt.

Runs have been made on polycrystalline specimens of tin of about 4-9's purity. Theoretical considerations indicate that the tin must be at least 6-9's pure before the effect of impurities on the kinetics is sufficiently small to be negligible. The data was taken over a velocity range of 10^{-5} to 10^{-3} cm/sec. and at undercoolings from 10^{-3} to 10^{-1}°C. A computer program was written to speed analysis of the data.

If the PTFE crucible proves satisfactory, the next step will be to perform experiments using single crystals of 6-9's pure tin.

Publications:

H. P. Utech and J. G. Early, On the Presence of Thermal Convection in the Kinetics Experiment of Rigney and Blakely; accepted for publication in Acta Metallurgica.

H. P. Utech, R. L. Parker, J. G. Early and S. R. Coriell, The Cam Equation for a Thermal Wave Generator; accepted for publication in Journal of Applied Physics.

2.2 Characterization of Electrodeposited Crystals

F. Ogburn, J. Smit

Electrolysis and Metal Deposition Section

The mid Fy 1967 progress report noted morphological particulars of the acicular form of electrodeposited silver crystals. Of special note was the observation that, without exception, all of the acicular crystals examined were twinned. Evidence of this was obtained from optical goniometric, x-ray diffraction and metallographic examinations of the specimens. Now data on large, i.e. over one cm long, electrodeposited prismatic and equiaxial form silver crystals, particularly with respect to twinning, is being sought by us.

The ease with which acicular silver crystals of over one cm length were obtained suggested that the techniques used to produce them would be a good starting poing for developing techniques for growing large single crystals of silver. Accordingly, during much of this reporting period that approach has been used in exploring the problems of large crystal growth.

There seems to be little difficulty in electrodepositing bulk form silver crystals of a few mm in size. The problem is to grow crystals individually in a compact form and to obtain large sizes without the appearance of extraneous growths. During the past few months we have made progress towards determining the reasons for the difficulties encountered. Chief among these are the existence in solution of organic impurities and microscopic particles of metallic silver from the corroding anodes and the improper balancing and control of concentration gradients, potential gradients and current density.

A beginning has been made on overcoming these difficulties. We are growing clusters of prismatic shapes several mm in length. Real success will probably come when we work out the techniques for isolating one crystal and continuing its growth without competition from other crystals.

2.3 The Crystallization Habits of Organic Polymers

F. Khoury and J. D. Barnes

Polymer Crystal Physics Section

Previous studies of the crystallization of poly(chlorotrifluoroethylene) from solution in poly(chlorotrifluoroethylene) oil have revealed that even at low supercoolings chain folded lamellar crystals are formed which are multisectored in character, i.e. they consist of a fine mosaic of fold domains (NBS Tech. Note 293, 1966; NBS Report 9406, covering the period July 1, 1966-January 1, 1967). Generally, this feature is observed only in polymer crystals grown from solution at relatively high supercoolings. In an attempt to examine whether in the case of polychlorotrifluoroethylene this feature is an inherent characteristic associated with the low tacticity of the polymer molecules as a consequence of which crystals of higher perfection cannot be grown irrespective of the degree of supercooling, or whether it is due in some manner to the solvent used in the above-mentioned study, an examination has been undertaken, andis still in progress, of the crystallization of the polymer from another solvent, namely 2,5-dichlorobenzotrifluoride.

Crystals grown from this solvent at different temperatures have so far been found to be multisectored. No evidence of the formation of six-sectored hexagonal lamellae having well-defined growth faces has been observed to date. Additional experiments with this solvent are being pursued.

Work has been initiated the object of which is to grow fibrillar crystals of polychlorotrifluoroethylene from solution using a technique due to Penning et. al. (Kolloid-Z. 205, 160, 1965), and to investigate the fine structural characteristics of these crystals with particular emphasis on the determination of the conformation of their constituent long chain molecules. Current efforts are aimed at establishing conditions under which the development of chain folded lamellar overgrowths on the surface of fabrillar crystals might be totally suppressed.

2.4 Homogeneous Nucleation Studies on Polymers

J. D. Hoffman, G. S. Ross and L. J. Frolen

Polymers Division

During the previous reporting period several narrow molecular weight samples were prepared from Marlex 50 and characterized. Using the improved techniques described in the previous report, three fractions have been examined (3,000, 6,000 and 23,000 MW). Isothermal nucleation as well as slow cooling and melting experiments at different rates have been conducted. The results are being analyzed to establish the effect of molecular weight on these types of material.

It is anticipated that studies on two high molecular weight fractions will be completed early in the next reporting period.

2.5 Kinetics of Crystal Growth from Solution

Richard Brooks and J. L. Torgesen

Inorganic Materials Division

Occlusion of mother liquor in solution-grown crystals leads to major physical and chemical defects which are often important whether the crystals are required for scientific purposes or for industrial use. Collection of further facts on the formation of inclusions of mother liquor, particularly in crystals of sodium chlorate and of ammonium dihydrogen phosphate, has led to formulation of a hypothesis which is consistent with observations made on crystals of several substances and which may be of wide applicability.

It was noted that occlusion of mother liquor sometimes follows a rise in the level of supersaturation. The mechanism depends on the surprising observation that if the supersaturation is high enough, crystal faces may develop hopper growth or other irregularities even when the solution is strongly stirred, if there is a relatively slight increase of supersaturation. If supersaturation is subsequently reduced, overgrowth of the irregularities can occur. In the case of crystals characterized by several forms, those faces which grow most rapidly, and which are normally observed only when super-saturation is small, are most liable to become irregular if supersaturation rises. These irregularities may be covered by continued growth of contiguous slow-growing faces without further change in supersaturation, or, if supersaturation falls again, they may be overgrown by faces of the kind originally present.

It is obvious that occlusion of mother liquor due to such causes can be discouraged or totally prevented by taking suitable action, which may differ in different cases; for example by avoiding abrupt fluctuations in growth conditions, by controlling supersaturation relative to the surface area of crystals, by designing crystallizers so that variation of crystallization within them are kept within limits, or by addition of habit modifiers which suppress formation of fast-growing faces.

2.6 Kinetics of Crystallization of Polymers from Solution and from the Melt

J. D. Hoffman, J. I. Lauritzen, Jr. and E. Passaglia

A complete analysis of all the published data on homogeneous nucleation, rate of growth from solution and from the melt, and melting point and lamellar thickness as a function of crystallization temperatures for polyethylene has been made. The older theories of Lauritzen and Hoffman, Frank and Tosi, and Price are unable to account for the observed data. The more general theory of Lauritzen and Passaglia[1] can account for all the data quantitatively, but even it necessitates that the lateral surface free energy have a slight temperature dependence. Once this is done all experiments including homogenous nucleation give the same value of end-surface free energy. This value is 75 ± 5 ergs/cm^2. A paper describing the analysis is complete

1. J. I. Lauritzen, Jr. and E. Passaglia, J. Research NBS 71A (1967).

2.7 Experimental X-Ray Atomic Scattering Factors

G. Burley

Crystallography Section

The final reduction of the data for the redetermination of the scattering factors of copper has been completed. The results were combined with a critical literature survey of previous results submitted for publication in the journal Acta Crystallographica.

Experimental x-ray intensity data for both ammonium chloride and high purity silicon have now been obtained. Data reduction is in progress.

2.8 Superconductivity Phenomena in Semiconductors

J. F. Schooley

Cryogenic Physics Section

Measurements have been made on the systems Bi(Sn) and Bi(Te) and on $Fe_x Co_y Si$ in collaboration with Texas Instrument Corporation and with Alloy Physics Section of NBS. Although all three systems represent plausible sites for superconductivity, none was found.

A paper written in Fall, 1966 in collaboration with Solid State Physics Section, NBS, "Superconductivity in Semiconducting $SrTiO_3$", J. F. Schooley and W. R. Thurber, Proceedings of International Conference on the Physics of Semiconductors, Kyoto, Japan, 1966 -Journal of Physical Society of Japan, Vol. 21, Supplement, 1966 has been published. A paper "Superconductive Properties of Ceramic Mixed Titanates", J. F. Schooley, H. P. R. Frederikse, W. R. Hosler, E. R. Pfeiffer , has been accepted for publication in the Physical Review. A third paper, "Superconducting Transition Temperatures of Semiconducting $SrTiO_3$", J. F. Schooley, W. R. Hosler, E. R. Pfeiffer, C. S. Koonce and M. L. Cohen has been accepted for publication in the Physical Review.

Preliminary measurements of the effect of hydrostatic pressure on the transition temperature of $SrTiO_3$ have been made. The effect is larger than that in superconducting tin, and may well be the largest known.

3. HIGH TEMPERATURE AND LASER MATERIALS

3.1 Diffusion in Refractory Materials

A. L. Dragoo, G. Gordon and J. B. Wachtman, Jr.

Physical Properties Section

A literature survey was conducted on diffusion studies of borides, carbides, nitrides and oxides of Be, Ti, Zr, Hf, Nb, Ta, Mo, Th and U. Particular attention has been given to oxygen diffusion in TiO_2 and the titanates, and additional information on diffusion-related properties of these compounds was obtained. Compilations of diffusion coefficients for the borides, carbides, nitrides and oxides of Be, Ti, Hf, Ta, and Mo have been completed.

The diffusion equation was solved exactly by means of Laplace transforms to provide a series of solution for the change in O^{18} enrichment of an oxide crystal as a function of penetration depth and time during diffusion. Four possible models were considered:

(1) Instantaneous equilibrium between the surface of an oxide slab of initial normal O^{18} content and an ^{18} enriched gas (O_2) of infinite volume;

(2) Instantaneous equilibrium and a finite volume of gas;

(3) A first order rate of exchange between the oxide slab and an infinite volume of gas;

(4) A first order rate of exchange and a finite volume of gas.

Currently the performance of an apparatus for diffusion studies of oxygen in single-crystal rutile is being evaluated. Research grade oxygen and O^{18} enriched oxygen from electrolysis of enriched water are being analyzed before and after passing through successive stages of the apparatus. The analyses are being performed with the isotope ratio mass spectrometer at the University of Maryland, which will be used throughout the oxygen diffusion experiments.

3.2 Deformation and Fracture of Ionic Crystals

S. Wiederhorn

Physical Properties Section

Measurement of the fracture energy of glasses of varied chemical composition has been initiated using the double cantilever technique.

It is hoped to relate the fracture surface energy to the Young's modulus of the glasses and so obtain a measurement of the internal strength of glass as a function of composition. The strength as a function of temperature is also being measured. The work is now about fifty percent complete and it is expected to have a report on the subject by the end of this period. Tentative results indicate the fracture surface energy to be only slightly dependent on temperature and chemical composition. This result is significant in that it reflects the importance of surface condition on the strength of glass and relegates chemical composition to a secondary role, i.e. how chemical composition effects other properties, resistance to chemical corrosion, resistance to abrasion.

In the next period, work will be initiated to determine the effect of aqueous environment on the fracture of glass. In particular the effect of various aqueous solutions on the static fatigue limit will be determined. This information will be of considerable practical importance, since in practice, it is this limit that limits the useful stresses that glass can sustain.

3.3 High Temperature Crystal Growth From Solvents

H. S. Parker

Crystal Chemistry Section

Research during this reporting period was primarily directed towards improving the limited success previously reported in the application of the temperature-gradient zone-melting technique to the growth of calcium molybdate (H. S. Parker, W. S. Brower, Growth of Calcium Molybdate Conf. on Crystal Growth, Suppl. J. Phys. Chem. Solids, pp. 489-491 (1967) February). Zone instability during the extended heating periods necesitated by the slow growth rates (about 5×10^{-3} cm/hr) was believed to be due to diffusion of lithium out of the molten zone. Efforts were directed towards minimizing diffusion by reducing the liquidus temperature on adding a third component to the calcium molybdate - lithium sulfate system while retaining the favorable liquidus slope. Investigation of liquidus temperatures in lithium-containing systems which appeared to have potential for reducing growth temperatures to below the 830° - 960°C temperature range indicated that the lithium sulfate - lithium chloride eutectic mixture (melting point 476°C) appeared suitable. Liquidus temperatures were of the order of 480° for compositions containing five weight percent calcium molybdate and 550° for those containing ten weight percent calcium molybdate.

Although the reported vapor pressure of lithium chloride indicated that volatility would become a problem at temperatures in the 800° range and above, it was felt that runs of reasonable duration could be expected in the 500° to 650° C temperature range. Growth experiments using the lithium chloride-lithium sulfate eutectic mixture as the solvent were largely unsuccessful. The volatility of the lithium chloride limited the duration of the growth period to 24-30 hours.

The severe restrictions imposed on the solvent by the temperature-gradient zone-melting technique as applied to complex oxides appear to limit the wider application of the technique to this class of materials. Obtaining sufficient solubility is not the major restriction, but the problem of obtaining a solvent which simultaneously meets the requirements of solubility, low volatility, liquidus temperature and suitable liquidus slope in order that the critical supersaturation required for growth can be obtained in a thin zone with the thermal gradients realizable in these materials is of major proportions. Even in those cases where a suitable solvent can be found, the maximum size of crystal obtainable is limited. In the case of calcium molybdate, it was found that if the thickness of the source material exceeded about 5-6 mm, the temperature of the heat source approached the melting point of the crystal to maintain a temperature of 900-860° at the zone. Attempts to use a tubular heat source and move the specimen necessitate the use of small diameter specimens if planar growth face and isotherms are to be maintained. For growth of more useful crystal sizes of oxides and other high temperature materials of high purity and high perfection, vapor growth techniques, either by vapor phase transport or by vapor phase reaction would seem more worthy of exploitation. These techniques would also offer a possible greater degree of control of the growth process through control of both the total pressure and the partial pressures of the reactants.

3.4 Crystal Characterization Studies by Optical Means

R. F. Blunt and M. I. Cohen

Solid State Physics Section

The study of electro-optical effects continues. Electro-reflectance spectra are being taken with the "Cardona" type apparatus and also electro-absorption measurements in the absorption edge regions.

The application of an electric field shifts (or in some cases, splits) the bands giving a very sensitive tool for the study of the electronic energy bands. Materials under investigation include oxides such as Cu_2O and TiO_2 and "perovskites" like $SrTiO_3$ and $BaTiO_3$.

The new vacuum-UV apparatus has been put into operation. Difficulties with the source currently limit operation to energies below about 9 ev (instead of 12 ev).

The emphasis at the moment is on a detailed study of the absorption edge of $SrTiO_3$; absorption and reflectively data [including results of ER (electro reflectance) measurements] are being analyzed. The ER data are taken on heavily reduced crystals. Most of the measurements are being carried out with polarized light on oriented specimens. This work should be ready for publication shortly.

During this period, a summary of the properties of three fluorides (CdF_2, PbF_2, and MgF_2) was compiled.

The optical properties of several other materials are being studied also. The list includes the zincblende crystals CuBr and CuCl; tetragonal scheelites $CaWO_4$, $PbWO_4$, and $PbMoO_4$; and the "perovskites" $CsPbCl_3$ and $LiNbO_3$. This latter class is of special interest owing to the "non-linear" optical behavior of amny of them. Some have inordinately large electro-optical coefficients making them of considerable current interest as possible light modulators for lasers.

3.5 Crystal Defect Studies Using Magnetic Resonance

Te-Tse Chang

Solid State Physics Section

The coaxial cable coupled microwave cavity (see report for period July 1, 1966 - January 1, 1967) has been completed. Difficulties were encountered with the vacuum seal at the junction of the cavity proper and the rest of the assembly. Usual ways of vacuum seal including indium gasket fail at low temperatures. This seal was finally achieved by enclosing the junction with a stainless steel can and soldered to the assembly. A manuscript is in preparation to report the design of this cavity and will be published.

A sample of Mo:TiO_2 1/2 x 8 x 10 mm was glued to the side wall of the microwave cavity at the place where the microwave magnetic field is maximum.

However, the sample was so thin that the microwave electric field is essentially zero there and the cavity mode will not be perturbed much, but the sample still has large enough volume to yield good signal for experimental observation. The signal was first saturated and then the recovery of the signal was visually observed with oscilloscope and recorded with photographic plate by multiple exposures. The sample was then removed from the cavity and coupled to the microwave waveguide directly to act as its own cavity. The relaxation processes were observed and recorded again. The corresponding results from both methods at 4°K, 3°K, and 2.11°K were carefully compared; there is no observable difference. This result clears the doubt which arose from the previous observation of the relaxation effect. The conclusion is that the nodes in the rutile cavity will not affect the relaxation processes. The reason might be due to the fact that the spin-spin relaxation between Mo ions is so fast that the spin termperature is uniform in the sample even at the spot where there is a node. A spin echo experiment is therefore recommended. An article concerning the relaxation effect of $Mo^{5+}:TiO_2$ is in preparation and will be published.

A preliminary measurement of the relaxation of $W^{5+}:TiO_2$ EPR signal has been performed. The result showed a tendency of oscillatory temperature dependence of the relaxation time. None of the existing theory will predict such behavior. However, the signal is weak, hence comparatively, the noise is high. Those factors make the measurement difficult. The reliability of the experiment result is doubtful. A precise and better means for measurement is on the program. The result will be reported later.

3.6 Semiconductor Laser Materials and Laser Device Studies

N. N. Winogradoff

Electron Devices Section

Scope - The work carried out included:

1. A comparison of the characteristics of:
   (a) diffused,
   (b) solution regrown[1], and
   (c) compensated vapour deposited epitaxial, GaAs injection lasers[2].

2. The evaluation of GaAs lasers made by incorporating a wide range of dopings (Sn, Te and Zn) and degree of compensation of the p type side of the junction with donors (Te)[2], by vapour phase epitaxy to determine optimum GaAs laser material specifications.

3. A study of the mechanisms responsible for the decrease in light power output with an increase in temperature in GaAs laser diodes.

4. The fabrication of an 11 diode, 50 watt room temperature GaAs laser array operating at 43 amperes.

Results and Conclusions - Reported in the above sequence).

1. Compensation of the p-type side of the junction with donors was essential for high power room temperature GaAs laser operation[2,3]. Although such compensation was present in both the diffused and solution regrown lasers, the compensation required for maximum light power output at low currents at room temperature was critical, and could best be obtained by vapour phase epitaxy. Such vapour phase epitaxial laser diodes produced substantially higher light output than similar solution grown lasers operating at the same temperature[4].

2. A contract for the production of a range of doped compensated $n/p^+/n^+$ vapour deposited epitaxial material made to our specifications, was placed with industry, and fourteen samples, some of which permitted comparison of the characteristics of lasers formed with epitaxial n^+p^+ layers and with epitaxial p^+ on Cochralski grown n^+ materials to be made, were received, and are being evaluated.

3. Using a focussed ruby laser beam incident on a crystal of GaAs to produce an excess carrier concentration in a highly localized hot area, it was shown that the decrease in light output of GaAs lasers at higher temperatures was mainly due to a decrease in internal quantum efficiency[5] and not to a change in internal absorption[6]. This conclusion is supported by independent field effect experiments[7] and by the dependence of the light output of GaAs p-n junctions on the junction width[8].

4. The laser array was passed on to Mr. W. Soper of the Harry Diamond Laboratories for application evaluations.

Personnel

N. N. Winogradoff (Group Leader), H. K. Kessler and K. Owen

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1. Nelson, H., and Dousmanis, G. C., Appl. Phys. Letters 4 192, 1964.
2. Winogradoff, N. N., and Kessler, H. K., Solid State Communications 2 119, 1964.
3. Winogradoff, N. N., and Kessler, H. K., Solid State Communications 5 155, 1967.*
4. Winogradoff, N. N., and Kessler, H. K., International J. Electronics 21 329, 1966.*

* New - based on work reported.

5. Winogradoff, N. N., Owen, K., and Curnutt, R., International J. Electronics (in the press) 1967.*

6. Gonda, T., Lamorte, M. F., Nyul, P., and Junker, H., IEEE QE2 74, 1966.

7. Winogradoff, N. N., Phys. Rev. 138 A1562, 1965.

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