(Fujian Inst. Res. Struct. Matter, Acad. Sin., Fuzhou, Peop. Rep. China). *Guisuanyan Xuebao* **1983**, 11(1), 95-104 (Ch). The Czochralski growth of $YAlO_3$ laser crystals doped with Nd or Nd and Cr was studied. The cracking and twinning caused by thermal expansion and structure anisotropy can be cor. by reducing the temp. gradient and improving the quality of the starting materials.

98: 189112k **Theoretical calculation of the composition of multicomponent equilibrium adsorption layers.** Ruzaikin, M. P (Sib. Fiz.-Tekh. Inst., Tomsk, USSR). *Mat. Metody Khim. Termodin., [Mater. Vses. Shk. "Primen. Mat. Metodov Opisaniya Izuch. Fiz.-Khim. Ravnovesii"], 3rd* 1980 (Pub. 1982), 63-70 (Russ). Edited by Kokovin, G. A. Izd. Nauka, Sib. Otd.: Novosibirsk, USSR. The Ga(111) and In(111) surfaces of GaAs and InAs crystals in the resp. gas-transport systems Ga-As-Cl-H and In-As-Cl-H are covered basically by at. Cl and As_4 mols. The growth of these surfaces is related to removal of surface Cl and surface reactions of Ga(GaCl) with As_4. The As(111) surface of GaAs crystals is covered mainly by As_4 mols. The nucleation and growth of nuclei is related to removal of As_4. This might be the reason for a slower growth of As(111) than that of Ga(111). A loose phase-dense phase transition is possible in adsorption layers on the As(111) surface of InAs crystal. The loose layer is composed mainly of As_4 and the dense layer of InCl. The different d. of the InCl adlayer causes a different surface kinetic coeff. and different crystal-growth rate.

98: 189143m **Study of induction systems for electromagnetic forming during the growth of silicon crystals.** Lev, L. R. (USSR). *Elektrotekhnika* **1983**, (2), 52-4 (Russ). The optimum conditions for the zone-melting growth of Si ribbons and plates in strong electromagnetic fields were studied. The ribbon or plate thickness is easily controlled by varying the field intensity. Thin, long ribbons with smooth surfaces are obtained.

98: 189144n **Formation of surface phases of chromium and epitaxy of chromium-silicon ($CrSi_2$) on silicon(111).** Lifshits V. G.; Zavodinskii, V. G.; Plyusnin, N. I. (Inst. Avtom. Protsessov Upr., Vladivostok, USSR). *Poverkhnost* **1983**, (3), 82-9 (Russ). The epitaxy of Cr on a Si(111) (7 × 7) surface was studied by LEED. The surface ordering changes as the degree of surface coverage θ increases. Initially, the (7 × 7) surface reconstructs to a (1 × 1) surface. At $\theta = 1$, a Si(111) - (7 × 7) -Cr structure appears. At θ 2 $\leq \theta \leq$ 8, a Si(111) - (7 × 7) - Cr + Si(111) ($\sqrt{3} \times \sqrt{3}$)-Cr structure appears due to 3-dimensional nucleation. At $10 \leq \theta \leq 28$, a $CrSi_2$ epitaxial film is formed with the (001) plane parallel to the Si(111) plane.

98: 189145p **Effect of electromagnetic forces on melt hydrodynamics in high-frequency floating-zone melting.** Liumkis, E.; Martuzane, E. (USSR). *Magn. Gidrodin* **1983**, (1), 116-24 (Russ). Fluid-dynamics calcns. were made of electrohydrodynamic effects induced in floating-zone melting by electromagnetic fields. Calcns. are given for the temp. gradients and flow lines in Si growth.

98: 189146q **Preparation of BP single crystals by high pressure flux method.** Kumashiro, Yukinobu; Misawa, Shunji; Gonda, Shunichi (Electroch. Lab., Ibaraki Prefect., Ibaraki, Japan 305). *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1983**, 51(1), 217-18 (Japan). Single crystals of BP, a III-V compd. semiconductor, were obtained by the high-pressure flux method. Cu_3P and $Ni_{12}P_5$ powders were used as the flux, and mixed with BP powder. Two kinds of mixts. were prepd.: (*1*) 1.8 g (BP) + 35 g (Cu_3P) and (2) 1.7 g (BP) + 25 g ($Ni_{12}P_5$). They were compressed into pellets, heated at 1300° for 24 h in an induction furnace under a pressure of 1 MPa using Ar-P_2 gas, and slowly cooled to room temp. In case (*1*), BP single crystals grew along the (111) plane, and in case (*2*) they grew as an aggregate of crystallites. The cathodoluminescence spectra of the synthetic BP crystals showed peaks near 680 nm (1.82 eV) for case (*1*) and 500 nm (2.47 eV) for case (*2*). S. Ueda

98: 189147r **Growth of new ferroelastic tantalum oxide (Ta_2O_5) single crystal.** Kojima, Hironao; Tanaka, Isao (Fac. Eng., Yamanashi Univ., Kofu, Japan 400). *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1983**, 51(1), 219-20 (Japan). Ta_2O_5 single crystals were prepd. from a sintered rod composed of Ta_2O_5 powder by using an IR imaging furnace. The growth rate was 0.5-4.0 mm/h in air or N_2 gas and the rotation of the shaft was 15-40 rpm. The single crystal had a cleavage along the (001) plane, and became colorless by annealing at 1000° in air. Penetration twins were obsd. in the cleavage plane and disappeared on heating at ≥430° but appeared again at room temp. These transition twins were related to a hysteresis of thermal expansion. From the migration of partial domains of twins by applying an external stress on the crystal surface, the single crystals are considered to be ferroelastic.

S. Ueda

98 189148s **Calcium phosphate crystallization. IV. Kinetics of heterogeneous nucleation of tetracalcium monohydrogen phosphate on brushite crystals.** Madsen, H. E. Lundager (Chem. Dep., R. Vet Agric. Univ., Copenhagen, DK-1871 Den.). *Acta Chem. Scand., Ser A* **1983**, A37(1), 25-9 (Eng). The kinetics of heterogeneous nucleation of OCP ($Ca_4H(PO_4)_3.2.5H_2O$) on brushite ($CaHPO_4.2H_2O$) at 37° was studied, partly by pH-static titrn. with $Ca(OH)_2$. Nucleation is strongly favored by crystal defects of the substrate. At const. supersatn. the rate of crystn of OCP is initially very low, thereafter being in accordance with the rate law. The stationary nucleation rate follows the classical (Becker Doering Volmer) expression, but the crit. nucleus contains only 1-2 formula units. The induction time t_i increases in steps with decreasing supersatn. This is most easily understood if it is assumed that t_i is not the induction time for nucleation, but rather a relaxation time of the crit. nucleus.

98: 189149t **In situ observation of monomolecular growth steps on crystals growing in aqueous solution. I.** Tsukamoto, K. (Fac. Sci., Tohoku Univ., Sendai, Japan 980). *J Cryst. Growth* **1983**, 61(2), 199-209 (Eng). By combining optical phase contrast microscopy with a conventional TV system, monomol. spiral growth steps on crystals can be obsd. during the growth in aq. soln. The image of the monomol growth steps is stored either in a video tape recorder or through an A/D converter into the floppy disk in a computer. The minimal step height on CdI_2 crystals measured by the in situ interferometry is ~1.4 nm, which satisfactorily agrees with the monomol. growth step height derived from the crystal structure. This observation method has a great advantage in understanding the growth mechs. of crystals in a more direct way when the growth rate measurement is coupled.

98: 189150m **An improved method for the measurement of the rates of growth and dissolution of crystals under isothermal conditions.** Rubbo, M.; Sherwood, J. N. (Dep. Pure Appl. Chem., Univ. Strathclyde, Glasgow, UK G1 1XL). *J Cryst. Growth* **1983**, 61(2), 210-14 (Eng). A volumetric method for the measurement of the isothermal growth and dissoln. kinetics of crystals is described. Its application to the growth of crystals of *n*-eicosane ($C_{20}H_{42}$) from soln. in *n*-dodecane ($C_{12}H_{26}$) is discussed, and the errors involved in the measurement are defined.

98: 189151n **Skull melter single crystal growth of magnetite (Fe_3O_4)-ulvospinel (Fe_2TiO_4) solid solution members.** Aragon, Ricardo; Harrison, Harold R.; McCallister, Robert H.; Sandberg, Charles J. (Purdue Univ., West Lafayette, IN 47907 USA). *J. Cryst Growth* **1983**, 61(2), 221-8 (Eng). A modified Bridgman technique by crucibleless skull melting was applied to the growth of equiaxed, cm-sized titanomagnetite $[(Fe_3O_4)_{1-x}.(Fe_2TiO_4)_x]$ single crystals, in O-buffered atmospheres. The relation between atm and spinel phase compns. was systematically investigated, through characterization by x-ray diffraction, polarized reflected light microscopy, and electron microprobe anal. Guidelines are discussed for generalization of the method to single crystal growth of ferrites of arbitrary compn.

98: 189152p **A refractometric method for continuous investigation of stirred crystal growth organic solutions.** Sigelle, M.; Flicstein, J.; Hierle, R.; Badan, J. (CNET PMS/PAB, F-92220 Bagneux, Fr.). *J Cryst. Growth* **1983**, 61(2), 229-34 (Eng) A continuous refractometric method with a He-Ne laser at λ = 6328 Å for investigating stirred crystal growth solns. is described. A measurement setup reliable for any long time running expt. was designed, which allows in situ nondestructive characterization of a 60 cm^3 vol. cell thermostated as ±0.01°. The theor. refractive index resoln. is $|\Delta n_{min}|_{th} = 3 \times 10^{-6}$, while the effects of room temp., atm. pressure, and beam waist broadening due to stirring flow birefringence are negligible. Only long time reproducibility considerations lead to an actual resoln. $|\Delta n|_{min} = 6 \times 10^{-6}$. The capabilities of the system were investigated using a well purified low satd. soln. of 3-methyl-4-nitropyridine 1-oxide-acetonitrile at a concn. C_0 = 2.37 × 10^{-2} mol/mol which is cooled from 34 to 20°. The method can be employed to follow any temp. programming, providing that the elemental segment is not less than $|\Delta T|_{min}$ = 0.015°, while concn. changes at const. temp. as low as ΔC_{min} = 0.03 g/L can be detected. No discontinuity around the soly. point at 29.5° was noticed.

98: 189153q **An experimental model of the flow in Czochralski growth.** Jones, A. D. W. (Sch. Math., Univ. Bristol, Bristol, UK BS8 1TW). *J Cryst Growth* **1983**, 61(2), 235-44 (Eng). An expt. was built to model the flow of the melt in Czochralski growth. Water and a mixt. of water and glycerol were used as the working fluids and the rates of rotation, temp. differences and dimensions of the app. were scaled so that the effects of rotation and buoyancy forces were correctly represented. Observations of the velocity and temp. fields are divided into 6 flow regimes. The investigation of the sep. effects of crystal rotation, differential rotation, and heating leads to a better understanding of the flows due to heating with crystal rotation and heating with differential rotation. It is expected that crystal rotational heating with differential rotation will occur during crystal growth.

98: 189154r **Analysis of silicon crystal growth using low pressure chemical vapor deposition.** Hottier, F.; Cadoret, R. (Lab. Electron. Phys. Appl., F-94450 Limeil-Brevannes, Fr.). *J. Cryst. Growth* **1983**, 61(2), 245-58 (Eng). The growth kinetics of Si films deposited under low pressure conditions ($Si-SiH_4$) system was investigated by using an exptl. reactor. Depending on the growth conditions, polycryst. or single-crystal films were obtained with different deposition kinetics. With the help of an ultra high vacuum chamber equipped with surface anal. facilities, which was directly connected to the reactor chamber, a detailed assessment of the growth interface was made. As shown by in situ ellipsometry, heating the substrate at a temp. >900° under an H flow induced a thermal etching of Si which could be counterbalanced by a low Si partial pressure. The stable state of growth for polycryst. or single-crystal film was also assessed by ellipsometry and addnl. information concerning the crystallinity or the crystal surface coverage of adsorbed mols. (mainly H) was obtained by using RHEED and AES techniques.

98: 189155s **Mechanisms of silicon monocrystalline growth from silane/molecular hydrogen at reduced pressures.** Cadoret, R.; Hottier, F. (Lab Cristallogr. Phys. Milieux Condens., CNRS, F 63170 Aubiere, Fr.) *J. Cryst Growth* **1983**, 61(2), 259-74 (Eng). The kinetics of monocryst. Si deposition on slightly misoriented {111}Si substrates from SiH_4 dild. in H_2 at reduced pressures was theor. analyzed in terms of a condensation process of Si atoms and SiH_4 mols., taking surface diffusion into account. The possibility of a homogeneous nucleation was considered by applying the classical

—コミュニケーション—

高圧フラックス法による BP 単結晶の作成

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The Preparation of BP Single Crystals by High Pressure Flux Method

Yukinobu KUMASHIRO*, Shunji MISAWA*, and Shun-ichi GONDA*

III－V族化合物半導体である BP は，高融点（～3000 ℃）で，バンド幅も広く（～2.1 eV），しかも *p*, *n* 両性の高温半導体に属する．筆者らは BP の新しい機能電子材料としての開発を進めるべく，その単結晶育成を行なっている．BP は高融点でありかつリンの蒸気圧がきわめて高く，1気圧では 1130 ℃ で $B_{13}P_2$ に分解し，2500 ℃ でリンの蒸発をおさえるには，94,500 気圧の超高圧を要する[1]．そのため直接メルトからの育成は不可能で，これまで育成された方法は CVD[2-5] 法，化学輸送法[6] およびフラックス[7-9] 法に限定されている．筆者らはできるだけ大きな単結晶を得ることを目標にして，独自な高圧フラックス法を適用して，従来の大きさのものが比較的短時間で得ることができた．本稿ではその結晶成長および評価の結果について述べる．

本実験で用いた方法は Chu[9] の石英封入管での金属リン化物メルトからの再結晶によって得た方法を，グラファイトるつぼ（内径 4 cm, 高さ 6 cm）を用い，高圧ふん囲気下で行なった．フラックスとして Cu_3P, $Ni_{12}P_5$ を用い (i) BP 1.8 g, Cu_3P 35 g, (ii) BP 1.7 g, $Ni_{12}P_5$ 25 g をおのおの別個に混合し，ペレット状に圧粉体に成型して，さらにリンを加えて，ADL 社製多目的結晶炉 (Fig. 1) を用い，Ar-P_2 10 気圧，誘導加熱により 1300 ℃に1日保持し，1～1.5日かけて徐冷を行なった．

徐冷後メルトの重量は原料挿入量より (i) の場合 2.2 g, (ii) で 1.8 g 減少していることから，一部は蒸発で失われていることがわかる．メルトを HF-HNO_3 中で溶解して結晶をとりだした．エッチングは溶融 KOH 中へ 8～10 分浸して行なった．

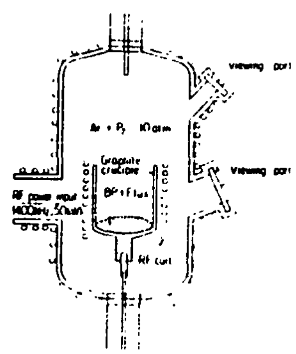

Fig. 1 Schematic illustration of crystal growth apparatus

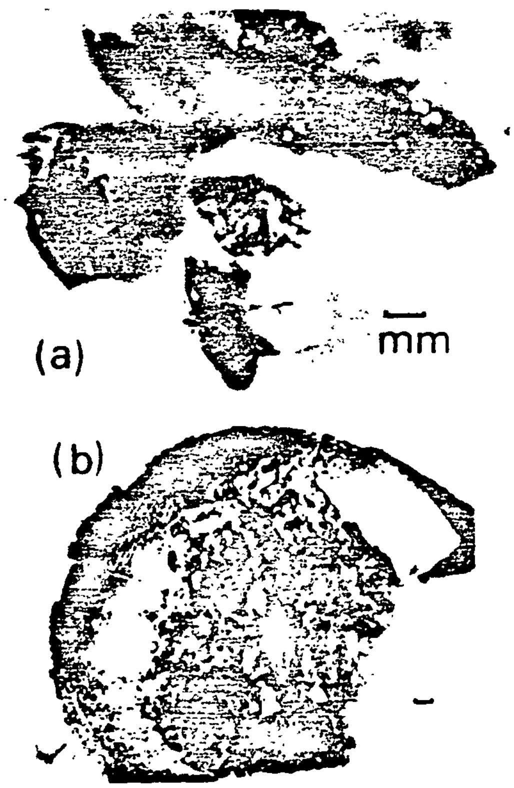

Fig. 2 BP single crystals by Cu_3P flux (a) and $Ni_{12}P_5$ flux (b)

得られた結晶の特徴は (i) では Chu[9] らの得たものより大きな赤色単結晶（Fig. 2 (a)）で自然面（111）[illegible]て成長していることが，X線ラウエ写真からわかる．(ii) では薄膜の上に大きな銀光沢で晶癖をもった単結晶の集合として成長している（Fig. 2 (b)）．

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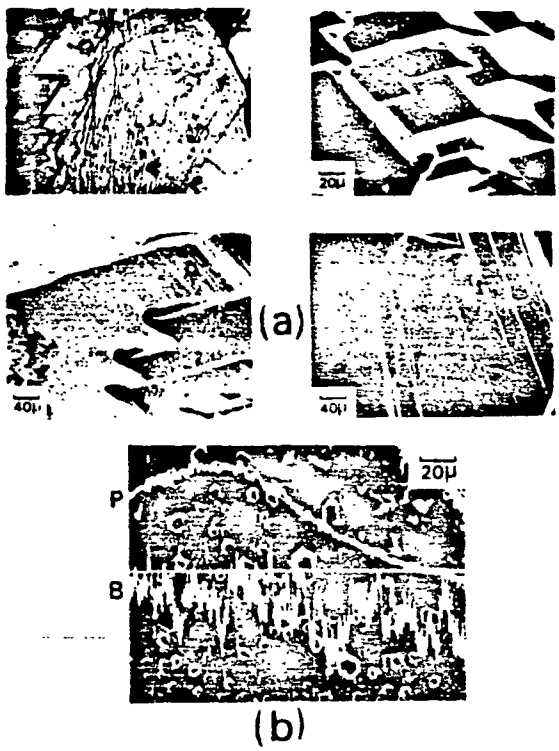

Fig. 3 Etching patterns of BP single crystals by optical microscope and scanning electron microscope. (a) Cu_3P flux (b) $Ni_{12}P_5$ flux. Also line profiles of B and P are shown

X線粉末回折によるといずれの場合でもフラックスおよび $B_{13}P_2$ の析出がみられる．後者についてはメルトの蒸発による減少から考えて，使用しているふん囲気圧力では，リンの蒸発は十分抑えきれないことを示す．(i) では a_0=4.538 A で文献値との一致はよいが，(ii) では $B_{13}P_2$ の析出（六方晶 a=5.98 Å，c=11.83 Å）が多く，格子定数が (i) より大きく a_0=4.542 A である．エッチングした結晶表面を光学顕微鏡および走査電顕で観察した結果を Fig. 3 に示す．(i) の結晶では（111）成長を示す三角形のほかに，ステップ，亜粒界を形成するピット列や液相成長法で得られたⅢ－Ⅴ族化合物半導体でみられる波模様[10]がみられる（Fig. 3 a）．(ii) の結晶は (i) と比較して多くの不規則な形状のエッチピットがみられ，X線マイクロアナライザーの線走査分析の結果からも $B_{13}P_2$ の析出に由来する組成のはらつきが大きい（Fig. 3 b）．

$Ni_{12}P_5$ フラックスでは Cu_3P よりも BP が溶解し，再結晶していることは Chu ら[9]の結果と一致するが，実験方式が異なるため，リンの蒸発は防げず $B_{13}P_2$ の析出が多くなり，BP 相に近い単結晶は得られにくい．

これらの結晶の基礎特性として，10 kV の電子線を照射させて，カソードルミネッセンスを観測すると，(i) では赤色発光し，(ii) では青色発光し，おのおの 680, 500 nm 付近にピークがあり（Fig. 4），エネルギーに直すと 1.82, 2.47 eV である．バンド間隔と合わせて考えると，(i) の場合文献値より大きく，Cu_3P に由来するものと思われ，(ii) では文献値より大きく，曲線の形状が非対称でピーク幅が広いことを考えると，$B_{13}P_2$ の発光 (3.1 eV) に由来するものと考えられる．

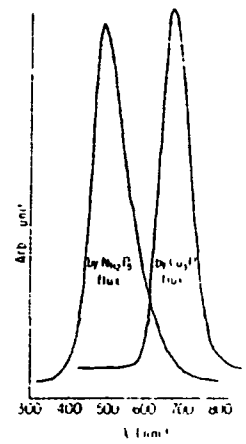

Fig. 4 Cathodluminescence spectra of BP single crystals

電気特性については，(ii) の薄層部分について Van der Pauw 法で測定すると，抵抗率 2.34×10^{-3} Ω·cm の p 型半導体で正孔濃度 2.48×10^{20}/cm^3，ホール易動度 11 cm^2/sV である．半導体特性についてはフラックスの $Ni_{12}P_5$ が影響をおよぼしていることがわかる．しかし易動度が比較的大きいことは，今後の結晶成長を遂行するにあたり，一つの指針が得られたと言える．

最後に本実験に協力頂いた法政大学卒研生 北井孝仁氏に深謝する

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