corresponds to a SiO_2 thickness of only ~3Å. At least 30 min elapsed between the time that the samples were cleaned and the time that they were put in the vacuum chamber of the accelerator. The same samples were measured by ellipsometry which indicated that a film thickness of ~40Å was present. In a separate series of experiments (8) it was verified that the prompt α-particle technique and ellipsometry gave the same results for oxide thickness >50Å, but diverged significantly for thinner layers.

The nature of this surface layer which appears ~40Å thick by ellipsometry, but yet contains only enough oxygen to comprise ~3Å of SiO_2 is not yet understood.

It can be seen that in those cases where the boron concentration was large, the oxygen concentration was also much larger. The additional oxygen which appears as a result of the solvent is ~10^3 times the additional boron concentration due to the solvent.

Conclusions

1. Methanol, acetone, and trichloroethylene leave measurable quantities of boron on the surface of Si samples. Reagent and electronic grade methanol are particularly bad, since they leave visible evaporation residue spots having concentrations as high as ~10^{14}/cm^2.
2. Chemical solvents can collect an existing uniform surface boron contamination into spots of much higher concentration.
3. The $^{18}O(p,\alpha)$ technique is a usable method of determining oxide thickness down to the 3Å range, even though ^{18}O is only 0.2% abundant.

Acknowledgments

We are grateful to A. C. Adams and R. H. Kaiser for making the ellipsometer measurements, to W. L. Brown for providing running time on the Van de Graaff, and to R. S. D'Angelo for technical assistance.

Manuscript received Oct. 1, 1973.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1974 JOURNAL. All discussions for the December 1974 Discussion Section should be submitted by Aug. 1, 1974.

REFERENCES

1. E. C. Lightowlers, J. C. North, A. S. Jordan, L. Derick, and J. L. Merz, *J. Appl. Phys.*, **44**, 4758 (1973).
2. F. Ajzenberg-Selove and T. Lauritsen, *Nucl. Phys.*, **11**, 45 (1959); *ibid.*, **11**, 117 (1959).
3. J. H. E. Mattauch, W. Thiele, and A. H. Wapstra, *ibid.*, **67**, 32 (1965).
4. R. E. Segal, S. S. Hanna, and R. G. Allas, *Phys. Rev.*, **139**, B818 (1965).
5. G. Amsel and D. Samuel, *Anal. Chem.*, **39**, 1689 (1967).
6. D. Strominger, J. M. Hollander, and G. T. Seaborg, *Rev. Mod. Phys.*, **30**, 585 (1958).
7. H. E. Schiott, in "Ion Implantation," F. H. Eisen and L. T. Chadderton, Editors, p. 197, Gordon & Breach Science Publishers, Inc., London, New York, Paris (1971).
8. J. C. North A. C. Adams, and R. H. Kaiser, Unpublished work.

Etching Solution for Revealing P-N Junctions in PbS and $PbS_{1-x}Se_x$

H. Preier and H. Pfeiffer

AEG-Telefunken Forschungsinstitut, D-6000 Frankfurt am Main, Germany

Lead salts are of great interest as materials for light detection and light emission in the infrared region. The p-n junctions of such laser and detector diodes are mainly fabricated by diffusion. However, thus far no etchants have been reported which optically display p-n junctions in lead salts. Here we will report about an etching procedure for revealing p-n junctions in $PbS_{0.6}Se_{0.4}$ and PbS. The composition of the room temperature etch is as follows: 40 ml deionized H_2O, 1.5g $K_2Cr_2O_7$, 10 ml HCl (37%), 1.5 ml H_3PO_4 (85%). Before use, this etching solution was diluted in water (2 parts water, 1 part etchant).

An example for an etched p-n junction in PbS is shown in Fig. 1a. Here an n-type crystal grown by sublimation from the vapor phase with the carrier concentration of 3 × 10^{18}/cm^3 (77°K) was diffused in sulfur rich PbS powder ($Pb_{0.49}S_{0.51}$) at 550°C for 1 hr. Diffusion and etching occurred perpendicular to as-grown (100) faces. Before etching, the crystal was embedded in an epoxy resin and mechanically polished to remove the p-layer from the exposed (100) surface. For chemical polishing an etching procedure was used which was described recently (1). The embedded crystal was then dipped into the etching solution for 3-5 sec and afterwards was quickly rinsed in deionized water and methanol. As can be seen from Fig. 1 p-type PbS is more strongly attacked by the etchant. Therefore, the junction is revealed by the step which occurs between the p- and n-region as shown in Fig. 1a. The variation of the thermoelectric power across the sur-

Key words: PbS, $PbS_{0.6}Se_{0.4}$, etchant for revealing p-n junctions, IV-VI compounds.

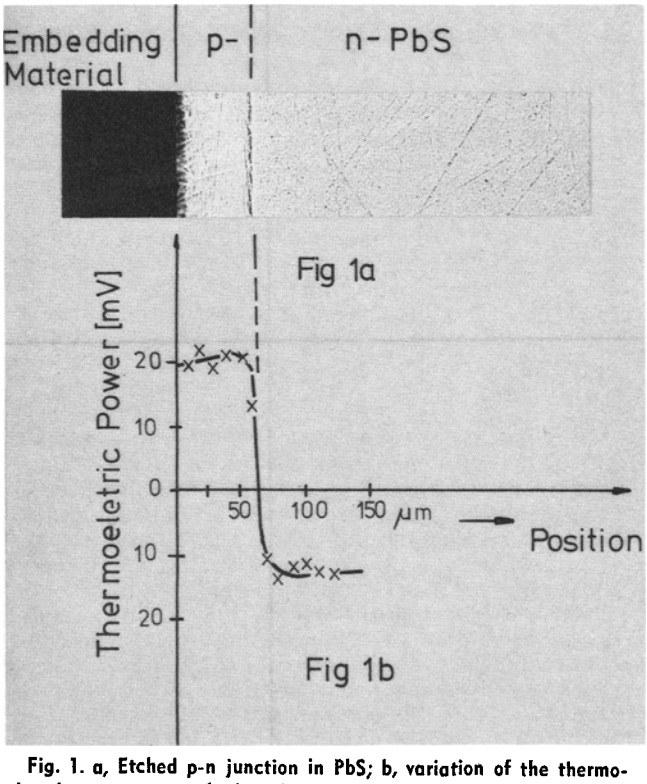

Fig. 1. a, Etched p-n junction in PbS; b, variation of the thermoelectric power across the junction.

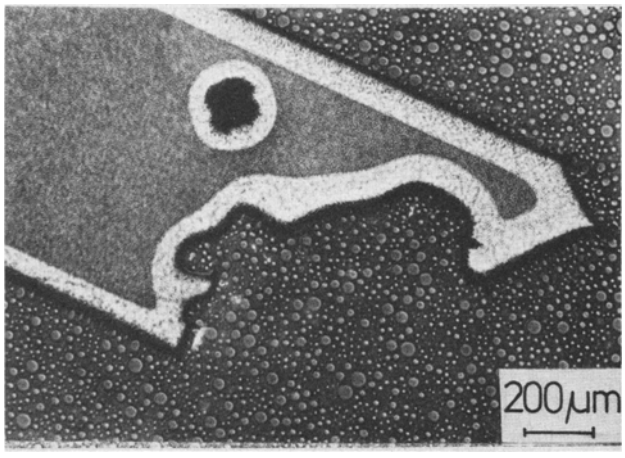

Fig. 2. Etched n-type $PbS_{0.6}Se_{0.4}$ crystal after diffusion in chalcogenide rich powder.

face of the etched PbS crystal was used as a controlling experiment for revealing the actual position of the p-n junction. The corresponding result is shown in Fig. 1b. A change of the sign of the thermoelectric power occurs exactly at the position of the etched step. This proves the agreement of the step with the position of the p-n junction and the usefulness of this etchant.

The same etching solution was also successfully applied to ternary lead salts. Here an n-type $PbS_{0.6}Se_{0.4}$ crystal with a carrier concentration of $4 \times 10^{18}/cm^3$ was diffused in ($S_{0.6}Se_{0.4}$) rich vapor at 550°C for 2 hr. An etched p-n junction in an irregularly shaped crystal is shown in Fig. 2. As can be seen, diffusion occurred also from a defect of the crystal surface. The junction depth as measured by thermal probe at 77°K was here about a factor of two smaller than the one revealed by etching. The latter effect is not fully understood yet and is presently being studied in detail.

Acknowledgment

This work was financially supported by the Ministry of Research and Technology of the Federal Republic of Germany as part of its technology program. The authors alone are responsible for the content of this paper.

Manuscript received Nov. 19, 1973.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1974 JOURNAL. All discussions for the December 1974 Discussion Section should be submitted by Aug. 1, 1974.

REFERENCE

1. G. A. Ferrante, M. C. Lavine, T. C. Harman, and J. P. Donnelly, *This Journal*, **120**, 310 (1973).

The High Pressure Crystal Growth of Sodium Beta-Alumina

F. H. Cocks

Duke University, School of Engineering, Durham, North Carolina 27706

and R. W. Stormont

Tyco Laboratories, Incorporated, Waltham, Massachusetts 02154

Sodium beta-alumina is of considerable interest because of the high mobility of its sodium ions (1-4). Indeed, it has been suggested that beta-alumina may be "a prelude to a revolution in solid state electrochemistry" (5). Such high ionic mobility makes possible, for example, its use as an ionic membrane separator material in high energy density batteries, such as the sodium-sulfur battery (6-9). Due to the highly anisotropic ionic conductivity of the beta-alumina crystal structure, single-crystal plates or tubes would result in membranes with improved conductivities and would also eliminate problems associated with the electrical short circuiting due to possible sodium metal diffusion along grain boundaries or through interconnected pores. For these reasons we addressed ourselves to the growth of single-crystal tubes of beta-alumina, oriented such that the high ionic conductivity planes of the resulting crystal are normal to the tube axis. There are considerable difficulties associated with the crystal growth of sodium beta-alumina, due principally to the fact that beta-alumina appears to decompose peritectically (10, 11) as well as to the high vapor pressure of sodium over beta-alumina at its decomposition temperature (11). In order to produce tubular crystals, we have made use of a recently developed crystal growth method called edge-defined, film-fed growth (EFG), which enables a variety of crystals to be grown having any constant cross-sectional shape (12-19). To counter the problem of sodium vaporization, a high pressure (300 psi), inert gas, EFG crystal growth chamber has been constructed, and to contain the reactive melt, both the crucible and the crystal-shaping dies were fabricated from iridium.

In the basic EFG procedure for crystals having a tubular shape, the liquid melt rises by capillary action to fill the feeding orifice in the tubular die (12-15). A seed crystal is then brought into contact with the melt at the top of the capillary feed slot. After adjustment of the melt temperature and seed withdrawal rate, the melt spreads across the top surface of the die until further spreading is prevented by the 90° change in contact angle at both the inner and outer edges of the die. The growth of a tubular shape from a thin liquid meniscus is then established.

The design of the high pressure EFG chamber needed to suppress sodium vaporization during growth is shown schematically in Fig. 1. A water-jacketed Type 304 stainless steel chamber comprises the basic pressure vessel. This vessel is fitted with two quartz viewing ports, each 4 in. in diameter. In addition, both x-y and linear feedthroughs enable the position of the crucible and EFG die to be controlled both vertically and horizontally. The crystal withdrawal mechanism is of standard design[1] and has a water-cooled shaft which can apply pulling rates between 0.01 and 10

Key words: beta-alumina, crystals, membranes.

[1] A. D. Little, Cambridge, Massachusetts, Crystal Withdrawal Mechanism No. 3637-Q35.