An Electron Microscopic Investigation of the Structure of Thin Film Tin Oxide Material

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Morphological structure of tin oxide thin films was examined by transmission electron microscopy. TEM samples were prepared by chemical etching in hydrogen fluoride solution: firstly floating for 2-3 minutes in acid solution, then suspending on water found to be useful for the preparation of TEM samples. Electron micrographs showed the size of grains of the tin oxide crystal was dependent upon the temperature of the film preparation. Dopant concentration and heating time also influence the grain size. The resistivity of tin oxide material was explained by grain size and grain boundaries in a limited temperature and dopant concentration ranges.

Introduction

SnO_2 is a main component of cassiterite mineral present in natural system. Since SnO_2 thin film was firstly made by oxidizing thin film of metallic tin in the air in 1937 by Bauer,[1] many chemists have been studying it because of characteristic properties of high conductivity and optical transparency.

SnO_2 can be classified as single crystal,[2-4] sintered material[5-6] and film[7-9] according to how it was prepared. SnO_2 is an intrinsically n-type semiconductor and it has about 3.7 eV band gap energy[10] at 0 K in the case of single crystal. By X-ray study,[11] it is known that SnO_2 single crystal is tetragonal rutile structure and its lattice parameters are a = b = 4.737Å, c = 3.185Å.

Semiconducting and transparent SnO_2 films were generally made by the use of hydrolysis,[12,13] reactive sputtering,[14,15] and vaccum evaporation[16,17] techniques.

It is known that such SnO_2 thin film has a little temperature effect on the resistivity and it is chemically stable[18] and also its structure is polycrystalline.[19] Allthough X-ray diffraction method is useful for the determination of crystal structure, it is not suitable for polycrystalline study.[20]

Transmission electron microscopy (TEM), on the other hand, has long been one of the main tools for the study of the growth of the thin film.[21] The morphology and geometry of the cyrstal structure can directly be observed by this technique. In the case of TEM, wavelength of electron is so short that the resolution is good and also the depth of field and the depth of focus are very large.[22]

In the case of thin film silicon, the relationship between electrical properties and grain size has been studied.[22-25] The electrical properties of polycrystalline silicon have been shown to be dependent upon the following parameters; the average grain size, the final processing temperature, the dopant heat of segregation and the entropy factor, the density of trapping states, and the height and width of grain-boundary barriers.[22] The average grain size of polycrystalline silicon is a dominant factor in its electrical properties. The theory and experiments showed that the resistivity was decreased with increasing grain size.[22-25]

Also information of local structure in micro scale with individual atomic level at or near the surface can be obtained with high resolution electron microscopy.[26] This HRTEM technique was used to elucidate the mechanism of compound formation and crystal growth in films of Cu and Se.[27]

It has been reported that the electrical property of thin film SnO_2 varies with preparation temperature,[28] heating time,[28] and dopant concentration.[29,30]

In this work, the relationship between the electrical properties of polycrystalline thin film SnO_2 and its structure, especially grain and grain boundaries was studied using TEM by changing the conditions at which SnO_2 thin films were prepared.

Experiments

1. SnO_2 Thin Film

(1) Reagents. Reagent grade chemicals without further purification were used. The substrate was 18mm by 18mm, 0.13 – 0.17mm thick coverglass which is the product of Corning Glass Works. Also 1/16 inch thick pyrex glass was used.

(2) Thin Film. These microscope slides were placed in soapy water to remove surface grease, rinsed with water, and wiped clean. Solution of 3M $SnCl_4$ in 3M HCl was sprayed. $SbCl_3$ was used as dopant.

After the coverglass substrate was placed on the heating plate which temperature was controlled and maintained within ± 10°C of the preset value by the temperature controller, spray solution was sprayed onto it. Spraying time was about 4 seconds. The glass substrate was removed from the heating plate after five minutes. The color of the thin film was pale brown. Its thickness is thought to be less than 1000Å from interference color point.[31]

2. SnO_2 TEM Specimen

(1) Chemical etching using HF solution. Glass(SiO_2) is etched by the chemical reaction with HF, $SiO_2 + 4HF = SiF_4(g) + 2H_2O$.

For the preparation of SnO_2 TEM specimen, the backside of the coverglass was etched with a small smooth brush using hydrofluoric acid(46%). Successive etching process is shown
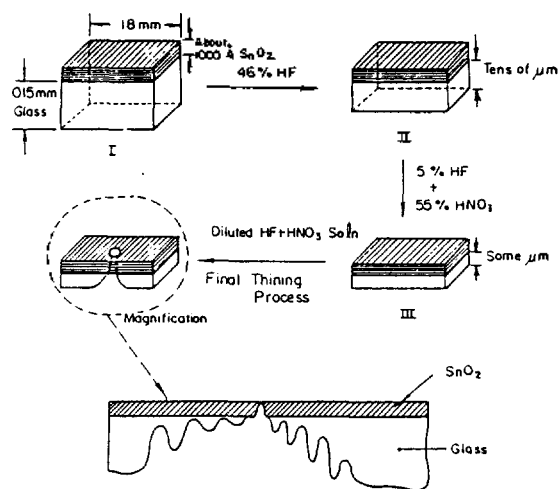
Figure 1. Schematic etching process of Tin Oxide thin film.

Figure 2. Schematics of lattice imaging procedure.

schematically in Figure 1. As the depth of the etching increased, diluted HF with HNO₃(1:3) was used to avoid severe chemical etching of SnO₂ by HF. In final stage, very diluted HF + HNO₃ (1:10) solution was used very carefully. At any moment, a small hole in the SnO₂ thin film was observed through magnifying glass (3X). At this point, etching was stopped immediately and washed with water. The region around the hole looked like a soft film. This part was placed above beaker with filled water and pierced with a small needle. Then the soft film part fell apart and was floating on the water. The thin glass containing SnO₂ film was ladled with an 80 mesh copper grid. Another grid was placed on top of the grid with sample to form a sandwitch and the double grid sample was kept in a sample box until it is ready for examination with TEM.

(2) Preparation of SnO₂ thin film by ladling with care. After SnO₂ sample was dipped into 5% HF + 55% HNO₃ solution for 2-3 minutes, this coverglass was slowly dipped into a beaker containing water. Then white SnO₂ thin film was afloat on the water. This floated film was ladled with 150 mesh copper grid and was kept in the sample box after removing water with paper tissue.

(3) Use of NaCl pellet as substrate. NaCl granule was ground for an hour in a mortar and again ground finely in an IR mortar for 30 minutes. This powder was used to make a clean surface NaCl pellet (1mm thick, 2cm diameter) at 500 Kg/cm³. After spray solution was sprayed on the NaCl substrate as before, the NaCl substrate sample was dipped into water. Then the SnO₂ thin film was afloat immediately after dipping. This thin film was netted with a grid and was kept in the sample box.

3. *Transmission Electron Microscope*

Photographing process of TEM is shown in Figure 2.[33] When the preliminary arrangement was completed, the specimen on the specimen holder was inserted. At first the specimen was observed and identified at low magnification then TEM pictures were taken at high magnification. A JEOL JEM-100C was used.

4. *Data Treatment*

Electron micrographs and transmission electron diffraction patterns were obtained using TEM with 100,000X magnification. From the micrographs, certain criteria on the grain were established that grain boundary must be obvious and the shade
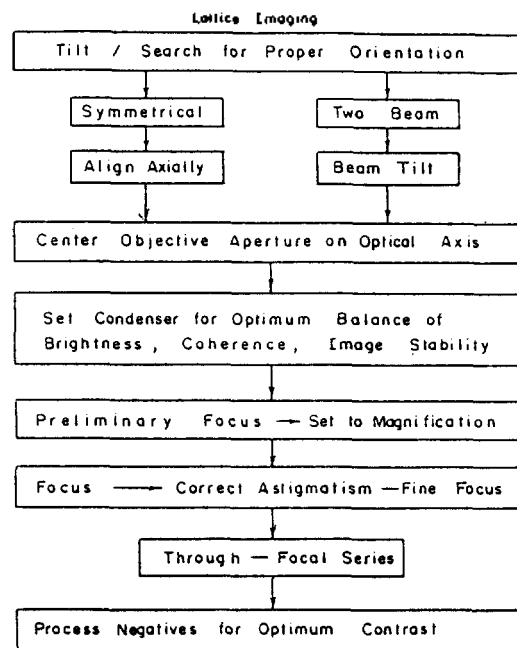
within grain must be homogeneous and the shade must be darker than some standard darkness. Grain size was measured using a Rotring ruler. Average grain size was calculated averaging about 20 various grains, of which 4-5 grains are larger ones, 4-5 grains smaller ones and 10-12 are medium ones.

Results and Discussion

Preparation of SnO₂ Specimen for TEM

In transmission electron microscopy, electron scattering is predominant due to the interaction of diffracted electrons with atoms. Therefore the thickness of the TEM specimen has to be within 1000 Å in 100 Kv acceleration.[20] In general, there are three methods for the preparation of the thin samples; electropolishing for conducting material,[33,34] ion thinning for nonconducting material,[23,34] and chemical etching for the both.[33]

Various preparation methods of SnO₂ thin film specimen were tried in order to prove the reliability of the floating method which was used mainly in this work. Chemical etching with a brush to the end and floating at the final stage did not show any difference from the floating method in terms of grain size and grain shape observed by electron micrographs. Thin film floating on 5% HF + 55% HNO₃ solution for 10 hours also shows the same results with the ones made by floating method. So, the thin film floating method is turned out to be useful for the preparation of SnO₂ TEM specimen because this method does not take long time, effort, and special care to have good results.

Even though NaCl substrate was used instead of coverglass, the results were almost the same. The TEM specimen with NaCl substrate could be easily obtained without etching with HF solution which was necessary for the glass substrates. Based on these results, reproducible grain size is observed with floating method since intact SnO₂ thin films can be obtained by different chemical etching methods. Ion bombardment after chemical etching could be a useful method at the final stage. A uniform thin film thus could be obtained.

Typical electron micrographs are shown in Figure 3. In Figure 3A, scattered circular spots are completely etched SnO_2 film while large black area is due to the glass substrate which blocks
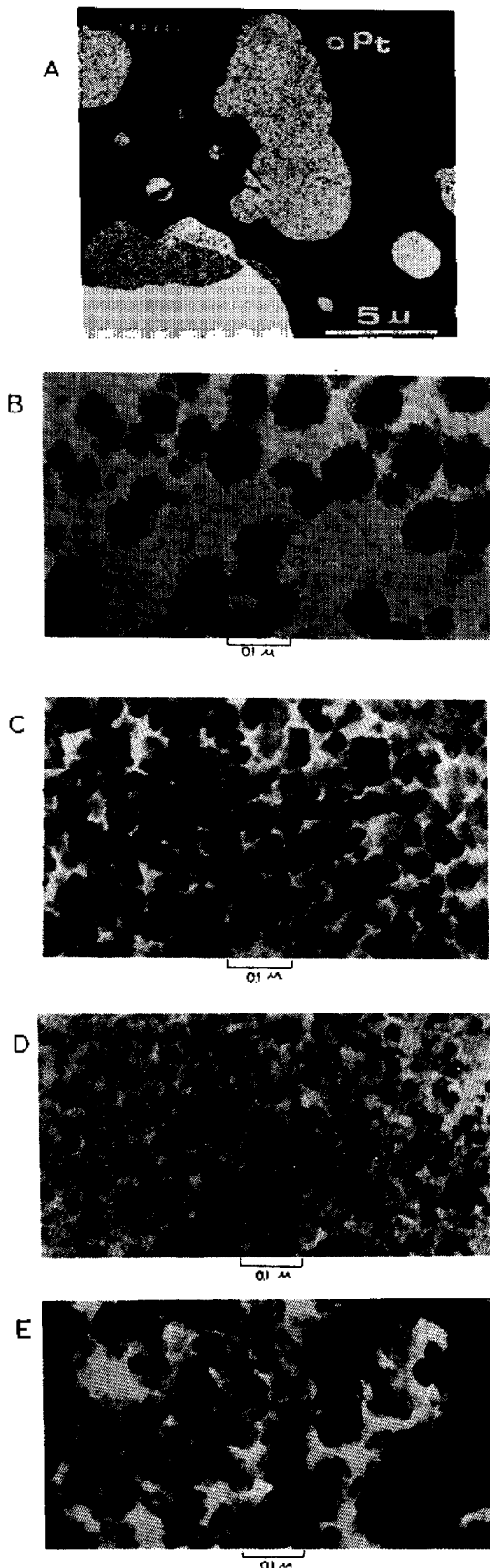
electron beams to penetrate. So high magnification TEM pictures were taken at one of the circular spots. Figures 3B through 3E were taken at samples prepared either at different temperatures or at different substrate. In Figure 3B, no clear crystals can be seen because of the amorphous nature of tin oxide made at 300 °C (see the following section). Also the crystalline structures are getting sharper as the temperature is increased. No difference in crystalline structure is observed in Figure 3E which was obtained from NaCl pellet substrate.

Relationship between Resistivity and Grain Size

In the case of silicon, average grain size is a dominant factor in determining its electrical properties such as film resistivity.[35] The average size of the grains has been shown to be a function of dopant concentration, thickness of the film, and preparation conditions such as temperature, heating time, and spraying speed.[36-38]

In general, it is believed that the grain size increases with temperature.[39] The temperature dependence on grain size is shown in Figure 4. The grain size increased with temperature between 300 °C and 400 °C in tin oxide samples with or without antimony. However, no further increase in grain size was observed at higher than 400°C temperature range. In order to verify that the above result is not due to the thermal inhomogeneity of the substrate placed on the hot plate, thick pyrex glass plates(1/16″) were used as substrates instead of coverglass. Since the thin substrates tend to warp while spraying because fo the thermal gradient, so the edges of the substrate were not in contact with the hot plate. But the observed grain sizes were the same no matter what thickness substrates were used. Therefore –

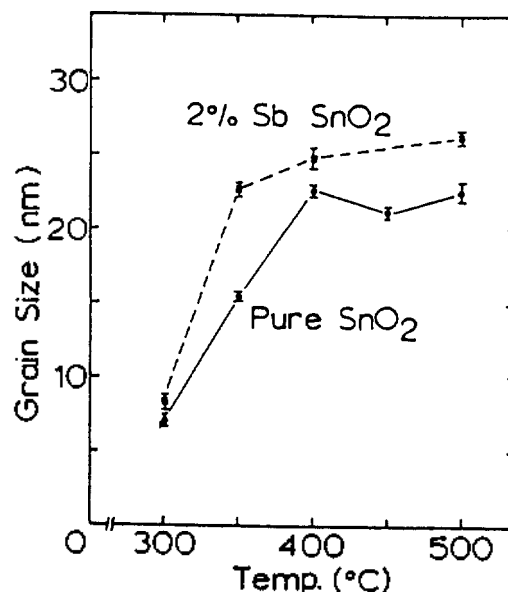**Figure 4.** Effect of temperature on grain size. ▮—▮ Pure Tin Oxide, ▮···▮ Tin Oxide with 2% Antimony.

Figure 3. Transmission electron micrographs of Tin Oxide without dopant. A: With low magnification prepared at 450 °C. B: At 300 °C. C: At 450 °C. D: At 500 °C, E: At 450 °C on NaCl substrate.

TABLE 1: Measured Grain Size(nm) at Various Dopant Concentration

Dopant (%)	Temp (°C)			
	300	350	400	500
0	7.0±0.2	15.2±0.6	22.7±0.9	22.4±1.1
0.5	—	10.8±0.7	—	—
2.0	8.2±0.2	22.9±1.3	25.2±1.5	26.9±1.0
5.0	—	31.4±1.5	—	—

it is concluded that the grains do not grow as rapidly as ones made at below 400 °C when the temperature is above 400 °C. When antimony is added, the thin film is reported to be more thermally stable.[39] In fact, it is difficult to make TEM specimen by floating the thin film for antimony doped SnO₂ samples. Arai reported that SnO₂ without any dopant was markedly unstable at low temperature.[18] Also annealing point of soft glass is 510 °C.[40] These two facts are related to the grain size in higher temperature (>400 °C) samples.

It is reported that conductivity of pure SnO₂ thin film decreases with the increasing temperature.[28] This phenomenon can be explained in terms of grain size. Pure SnO₂ single crystal is an insulator because of a large band gap energy. Randomly oriented nonstoichiometric grain and grain boundaries exist, however, in the case of polycrystalline tin oxide due to the oxygen deficiency[18] or tin atom interstitial.[41] Electrical current can flow not through grain, but through grainboundaries. Consequently, the relative number of grain boundaries decreases as the grain size increases[42] and therefore electrical current decreases. From the experimental results, this assumption was acceptable at lower temperature region below 400 °C. The higher the temperature is, the larger the grain size is and the less conductivity is.

In Table 1, the effect of dopant concentration in grain size is shown. When antimony was added, the grain size showed a positive dopant effect. Also in the case of polycrystalline silicon thin film it was reported that the grain size showed a positive dopant effect.[43] Cha[29] reported that the surface resistivity was decreased when antimony was added. The measured size showed a positive effect for antimony concentration, and a negative effect on resistivity.

This phenomena can also be explained in terms of grain and grain boundaries. The radius of $Sb^{5+}(0.62Å)$ is similar to that of $Sn^{4+}(0.74Å)$. So antimony ion can easily replace the Sn^{4+} ion site. This causes n-type extrinsic property when antimony is doped.

There are two possible reasons for grain growth depending on impurity concentration[44]; "liquid phase growth"[45] and "diffusion enhanced growth".[46] Liquid phase can't be found by TEM micrographs. So the diffusion enhanced growth in which an increase in diffusion coefficient enhances grain growth might be applied to antimony doped tin oxide. Therefore, although the grain size was increased when antimony was doped, the electrical current could flow easily by the extrinsic nature of semiconductor.[12]

The relationship between heating time and grain size is shown in Figure 5. The grain size increases with the heating time. It was reported that as the heating time increases, the resistivity increases.[28] This is because the surface Sn(II) is oxidized to Sn(IV),[47] thereby decreasing the oxygen deficiency and halides were replaced by oxygen.

In this case relationship between resistivity and grain size can also be explained as before. It was found that within limited temperature and dopant concentration, such relationship was observed. Moreover antimony doped SnO₂ thin film showed a good relationship even at relatively high temperature and high dopant concentration. In Figure 6, successive heating effect can
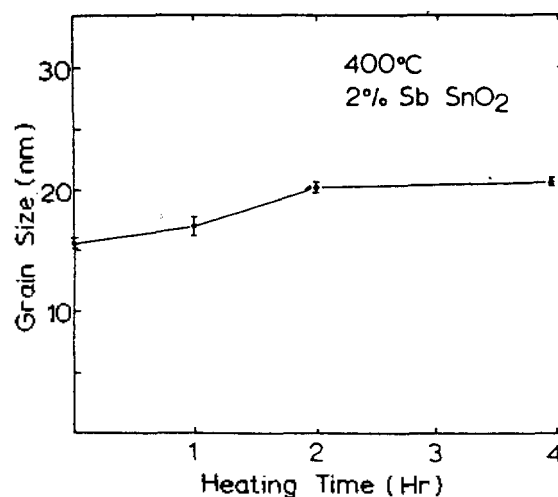
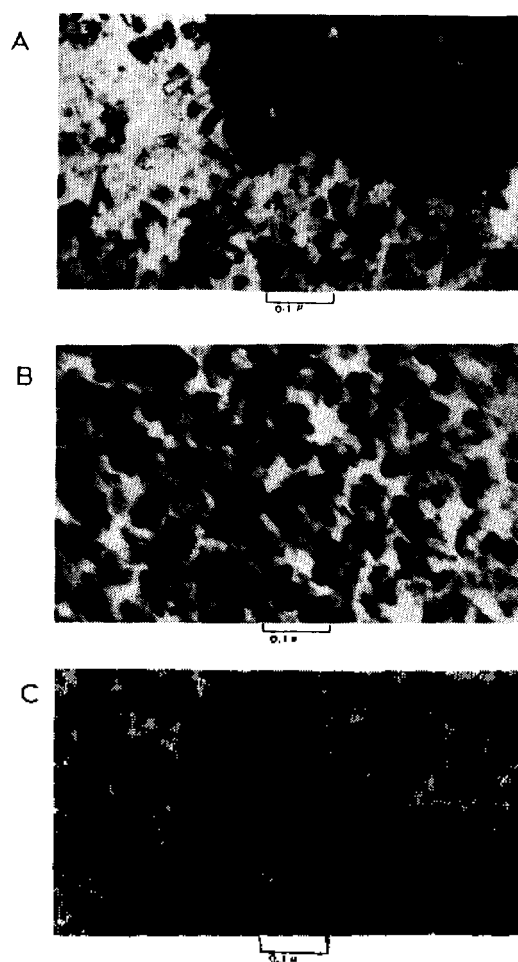**Figure 5.** Effect of heating time on gain size on Tin Oxide with 2% Antimony made at 400 °C.

Figure 6. Transmission electron micrographs of 2% Antimony doped Tin Oxide made at 400 °C. A: Immediately after preparation, B: Heating for 1 hour at 400 °C, C: Heating for 4 hours at 400 °C.

be seen with the sample prepared at 400 °C. It shows the crystallinity is getting crispier as the heating is continued.

Transmission Electron Diffraction Pattern

Electron diffraction pattern varies with the grain size as shown in Figure 7. As the grain size increases the breadth of ring becomes sharper which is the characteristic of electron diffraction. From these results, the crystallinity can be verified by transmission electron diffraction micrographs.
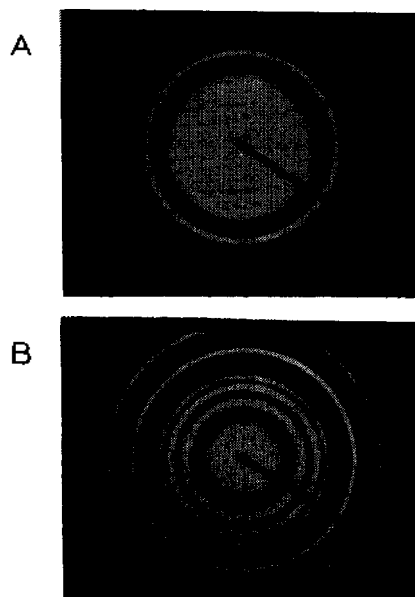
Figure 7. Electron diffraction pattern of Tin Oxide. A: Made at 300 °C, B: Made at 500 °C.

Determination of Critical Temperature from Amorphous to Polycrystal Structure

When the temperature is low enough as shown in Figures 3B and 7A, the grain size is small and its electron diffraction pattern shows halo form which is the characteristic of amorphous crystal. So it can be suggested that the critical temperature of transformation from amorphous to polycrystal tin oxide is a little below than 300 °C. Arai[18] reported that reversible change under 250 °C and irreversible change above 250 °C took place by plotting resistivity of Nesa as a function of 1/T.

References

(1) G. Bauer, *Ann, Physic. (Leipzig)*, **30**, 433 (1937).

(2) J. A. Marley and T. C. Macavoy, *J. Appl. Phys.*, **32**, 2504 (1961).

(3) T. B. Reed, J. T. Roddy, and A. N. Mariano, *ibid.*, **33**, 1014 (1962).

(4) M. Nagasawa, S. Shionoya, and S. Makishima, *Japan J. Appl. Phys.*, **4**, 195 (1965).

(5) H. J. Van daal, *Solid State Commun.*, **6**, 5 (1968).

(6) H. E. Matthews and E. E. Kohnke, *J. Phys. Chem. Solid*, **29**, 653 (1968).

(7) K. Ishiguro, T. Sasaki, T. Arai, and I. Imura, *J. Phys. Soc. Japan*, **13**, 296, 755 (1958).

(8) I. Viscrian and V. Georgescu, *Thin Solid Films*, **3**, R17 (1974).

(9) E. Giani and R. Kelly, *J. Electrochem. Soc.*, **121**, 394 (1974).

(10) E. E. Kohnke, *J. Phys. Chem. Solids*, **23**, 1557 (1962).

(11) W. H. Baur, *Acta Cyrst.*, **9**, 515, (1956).

(12) R. F. Aitchison, *Australian J. Appl. Sci.*, **5**, 10 (1954).

(13) J. A. Aboaf and V. C. Marcotte, *J. Electrochem, Soc.*, **120**,

(14) L. Holland and G. Siddal, *Vaccum*, **3**, 375 (1953).

(15) W. R. Sinclair and F. G. Peters, *J. Electrochem. Soc.*, **112**, 1096 (1965).

(16) H. A. Klasens and H. Koelmans, *Solid State Electron.*, **7**, 701 (1964).

(17) W. Spence, *J. Appl. Phys.*, **38**, 3767 (1967).

(18) T. Arai, *J. Phys. Soc. Japan*, **15**, 916 (1960).

(19) Z. M. Jarzebski and J. P. Marton, *J. Electrochem. Soc.*, **123**, 202C (1976).

(20) N. B. Hannay, "Treatise on Solid State Chemistry", Vol. 3, p. 170, Plenum Press, New York (1976).

(21) D. W. Pashley, *Advan. Pyhs.*, **14**, 327 (1965).

(22) P. Hirsch,, A. Howie, R. Nicholson, D. Pashley, and M. Whelan, "Electron Microscopy of Thin Crystals", pp. 24-65, Butterworths, London (1965).

(23) R. Castaing, *Rev. Metall.*, **52**, 669 (1965).

(24) R. Phillips, "Techniques for Electron Microscopy", Chap. 10, Ed. by D. Kay, Oxford, Bladewell (1965).

(25) M. M. Mandurah, *IEEE Transactions on Electron Devices*, Vol. Ed. **28**, No. 10, 1163, 1171 (1981).

(26) L. R. Eyring, *Ultramicroscopy*, **8**, 39 (1982).

(27) M. Shiojiri, C. Kaito, Y. Saito, K. Teranishi, and S. Sekimoto, *J. Crystal Growth*, **52**, 882 (1981)

(28) H. Kim and H. A. Laitinen, *J. American Ceramic Soc.*, **58**, 23 (1975).

(29) H. K. Cha, M. S. Thesis, Seoul National University, Seoul, Korea (1980).

(30) A. F. Carroll and L. H. Slack, *J. Electrochem. Soc.*, **123**, 1889 (1976).

(31) J. M. Mochel, *U. S. Patent Office*, 2564707 (1951).

(32) G. Thomas and M. J. Goringe, "Transmission Electron Microscopy of Materials", p. 45, Wiley Interscience, New York (1979).

(33) P. A. Jacquet, *Met. Review*, **1**, 156 (1956).

(34) W. J Tegart, "Electrolytic and Chemical Polishing of Metals", Pergamon Press, London (1982).

(35) Ref. 25, p. 1172.

(36) Y. Wada and S. Nishimatsu, *J. Electrochem. Soc.*, **125**, 1499 (1978).

(37) M. M. Mandurah, K. C. Saraswat, and T. I. Kamins, *Appl. Phys. Lett.*, **36**, 683 (1980).

(38) M. M. Mandurah, K. C. Saraswat, and C. R. Helms, *J. Appl. Phys.*, **51**, 5755 (1980).

(39) Ref. 22, p. 48.

(40) M. D. Briton, *Angew. Chem. Int. Ed.*, **15**, 346 (1976).

(41) W. D. Kingery, "Advances in Ceramics", Vol. 1, p.2, The American Ceramic Society, Columbus (1979).

(42) Ref. 20, Vol. 5, p. 119.

(43) Y. Wada, *J. Electrochem. Soc.*, **125**, 1499 (1978).

(44) K. Lucke and K. Detert, *Acta Metall.*, **5**, 628 (1957).

(45) G. G. Kuczynski, ed, "Sintering and Related Phenomena", Proceedings of the 3rd International Conference on Sintering and Related Phenomena, Plenum, New York (1973).

(46) J. M. Fairfield and B. J. Masters, *J. Appl. Phys.*, **38**, 3148 (1967).

(47) C. A. Vincent, *J. Electrochem. Soc.*, **119**, 515 (1972).