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Studies on Thin Films of Antimony Vacuum Evaporated from a Knudsen-Type Source

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ABSTRACT

A Knudsen-type evaporation source was used for the deposition of thin films of antimony to study their growth and microstructure under different rates of evaporation and substrate temperatures when vacuum evaporated onto air-cleaved *KCl*, mica, amorphous carbon and doped *KCl* substrates. The crystallisation of these films on exposure to an electron beam of moderate intensity inside the electron microscope was studied, and the orientations of the crystallised films wrt the substrate were established. It has been concluded that antimony films prepared by this source compare well with those prepared by other sources of vacuum evaporation.

1. INTRODUCTION

Many metals and metallic oxide films have been reported to have an amorphous structure, which changes to the crystalline form on annealing or exposure to an electron beam[1]. Amorphous structure in vacuum evaporated antimony films and its transformation to the crystalline form by annealing is well known. However, the observations of formation of amorphous antimony films on crystalline substrates or their crystallisation on exposure to the electron beam have not been reported earlier [2-4]. A transmission electron microscope (TEM) study has been made on thin films of antimony evaporated onto air-cleaved *KCl*, mica, amorphous carbon films and highly doped *KCl* crystals at different substrate temperatures and rates of deposition. A Knudsen-type evaporation source was used for the vacuum deposition[5]. Also, the crystallisation of amorphous antimony films on exposure to an electron beam of moderate intensity (~20 μA total current) inside the electron microscope has been studied. The orientations present in the crystallised films wrt the substrate surface have also been established.

2. EXPERIMENTAL DETAILS

Antimony powder of 99.9999 per cent purity supplied by Koch-Light Ltd., England, was evaporated in a conventional vacuum chamber with a vacuum of the order of 10^{-5} Torr. (i.e.,1.33×10^{-3} Pascal). A Knudsen-type source having an effusion aperture was used as the source of the evaporant material. The rate of evaporation was varied by changing the temperature of the crucible by regulating the current in the tungsten spiral encircling it. The temperature of the substrate was kept constant by keeping it in thermal contact with the substrate heater. Evaporation was started when the temperature of the substrate had remained constant for about

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half-an-hour and the heating current was switched off as soon as the evaporation was over.

An aluminium shutter was interposed between the crucible and the substrate. This shutter could be operated mechanically from outside the vacuum chamber. The shutter was kept closed till the crucible had attained the required temperature and was opened only for the duration of evaporation. Very thin films were backed by carbon using the carbon coating technique of Bradley[6].

Films from *KCl* substrates were removed by floating off in distilled water and then picked up on standard electron microscope grids. From the mica substrates, the films were detached using the technique of Hermann and Reimer[7]. Transmission electron micrographs and the selected area diffraction (SAD) patterns were taken with the help of Siemen's Elmiskop 1 operated at 80 KV or 100 KV.

To study the effect of electron beam irradiation, the films were exposed to an electron beam of moderate intensity (~20 μA total current). For this purpose, the image of the films was formed on the screen using a fairly spread beam. The beam current was then increased in small steps, keeping the screen under visual observation for any apparent change. For determining thickness of the films, Tolansky's[8] interferometric method was employed. The results were cross-checked by microbalance weighing before and after deposition.

3. RESULTS

3.1 Evaporation onto *KCl* Substrates

3.1.1 *Substrates at Room Temperature*

Figures 1(a) and 2(a) show electron micrographs of antimony grown on air-cleaved *KCl* substrate at room temperature and at a rate of deposition ~ 10 Å/s. Figure 1(a) is the micrograph of antimony film (100 Å thick) and shows that a film is in the post-nucleation stage, while Fig. 2 (a) is the corresponding micrograph of an antimony film (250 Å thick) and shows that the film has attained electrical continuity. SAD patterns in the inset of Figs 1(a) and 2(a) show that both the films are microcrystalline. Parallel studies made on films grown under the same substrate conditions as above, but with a higher rate of deposition (~ 150 Å/s) show that an increase in the rate of deposition has no effect on the structure of the films either in the post-nucleation stage or when these films attain electrical continuity.

3.1.2 *Substrates at Elevated Temperatures*

Studies of films grown on *KCl* subsrates maintained at temperatures higher than 100 °C show that the films are invariably crystalline in nature irrespective of the rate of evaporation. Figures 3 and 4 are electron micrographs of two such films grown on *KCl* substrates kept at 250 °C and at a rate of

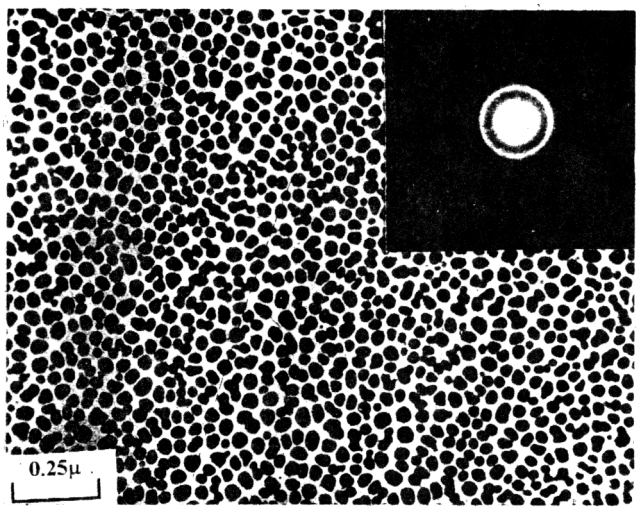

Figure 1(a). Antimony film (100 Å thick) deposited onto *KCl* substrate at room temperature and at a rate of deposition 10 Å/s.

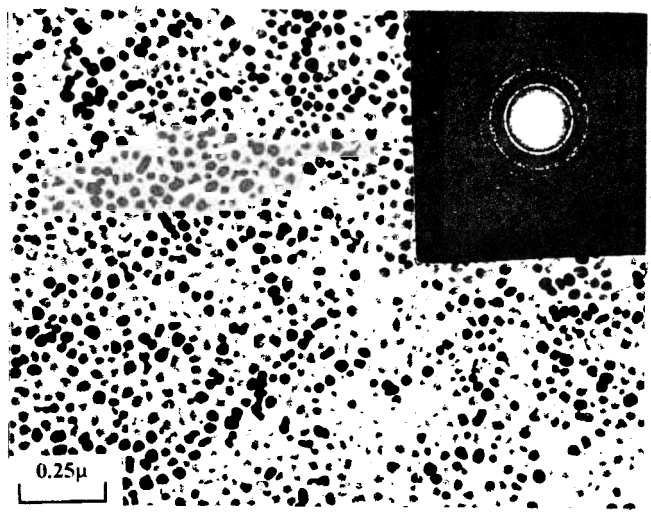

Figure 1(b). Antimony film of Fig. 1(a) after exposure to an electron beam of moderate intensity inside the electron microscope.

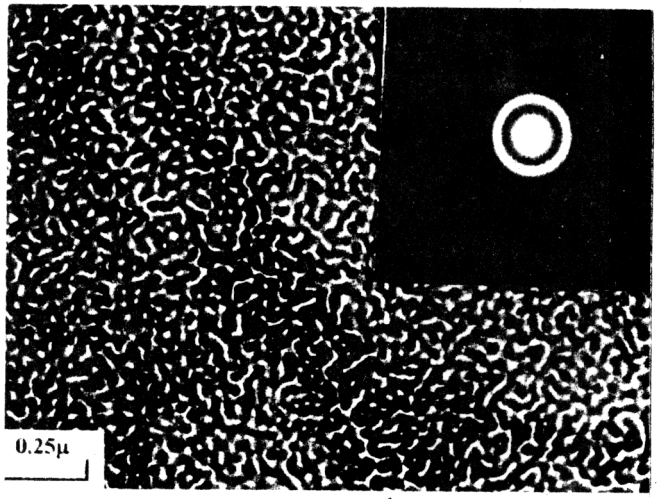

Figure 2(a). Antimony film (250 Å thick) deposited onto *KCl* substrate at room temperature and at a rate of deposition 10 Å/s.

deposition of about 10 Å/s. Figure 3 shows a film about 75 Å thick in the post-nucleation stage, while Fig. 4 shows a corresponding film about 400 Å thick, which has attained electrical continuity. SAD patterns in the inset of these figures show that both the films are polycrystalline, with preferred orientation.

Parallel studies on films grown on *KCl* substrates held at 250 °C but at a correspondingly higher rate of deposition show that films in the post-nucleation stage are polycrystalline, while the electrically continuous films take up a single crystal orientation. Figure 5 shows an antimony film 600 Å thick grown

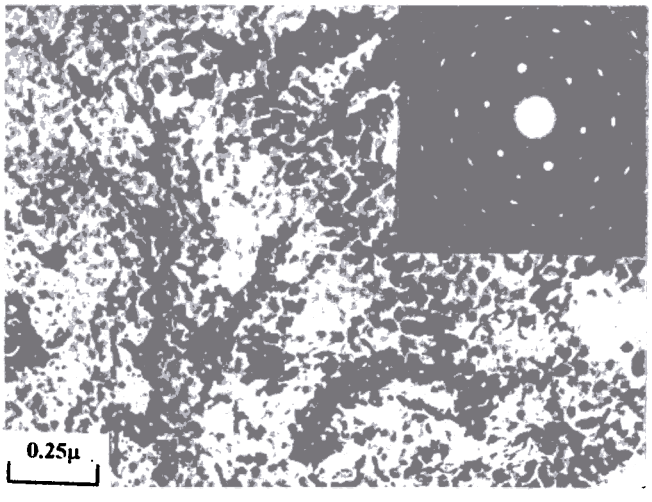

Figure 2(b). Antimony film of Fig. 2(a) after exposure to an electron beam of moderate intensity inside the electron microscope.

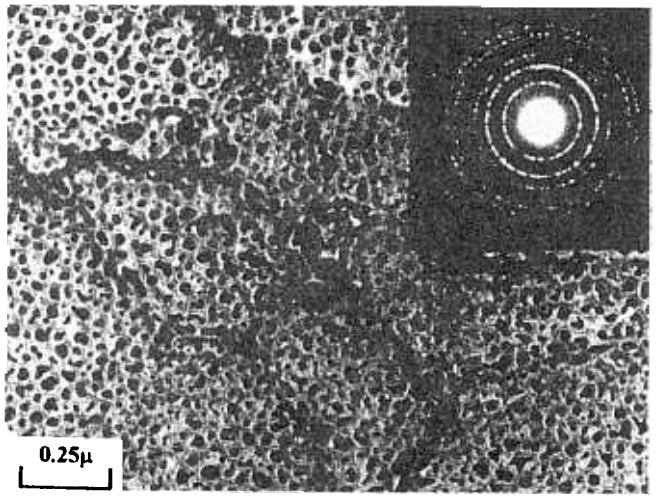

Figure 3. Antimony film (75 Å thick) deposited onto *KCl* substrate at 250 °C and at a rate of deposition 10 Å/s.

on *KCl* substrate heated to 250 °C and at a rate of evaporation of ~ 150 Å/s. Assuming a rhombohedral structure for antimony, the orientation of this film is $(111)_{Sb}$ // $(001)_{KCl}$.

3.1.3 *Electron Beam Irradiation*

Microcrystalline antimony films as obtained by evaporation onto room temperature substrates were irradiated in a 40 KV-100 KV electron beam of moderate intensity (~ 20 μA total current). It was observed that exposure to the electron beam results in transformation of these films to the crystalline form. Figure 1(a) shows a microcrystalline antimony

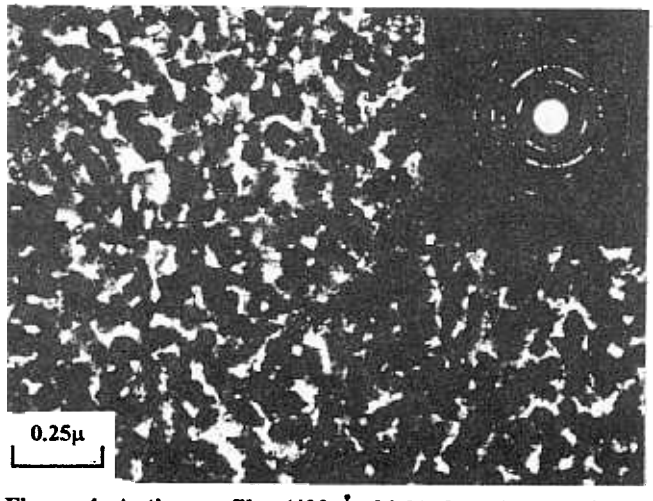

Figure 4. Antimony film (400 Å thick) deposited onto *KCl* substrate at 250 °C and at a rate of deposition 10 Å/s.

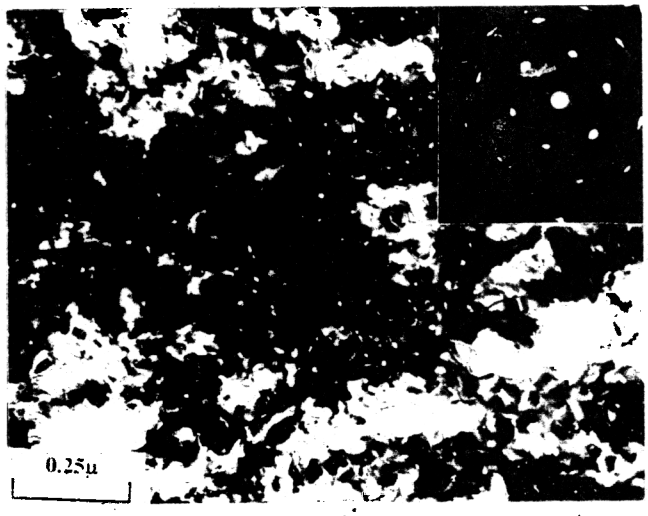

Figure 5. Antimony film (600 Å thick) deposited onto *KCl* substrate at 250 °C and at a rate of deposition 150 Å/s.

film in the nucleation stage ~ 100 Å thick before exposure to the electron beam, while Fig. 1(b) shows the same film after irradiation in the electron beam. SAD pattern shows that the film assumes polycrystalline structure after exposure to the beam. Figure 2 (a) shows an electrically continuous amorphous antimony film 250 Å thick before exposure to the electron beam, while Fig. 2(b) shows the same film after irradiation in the electron beam of the electron microscope. SAD pattern shows that the crystallised film assumes a single crystalline orientation, with some weak spots. The orientation of the film is $(111)_{Sb}$ // $(001)_{KCl}$

To confirm these results, the shutter between the source and the substrate was utilised to form a wedge-shaped film, which was backed by a carbon film about 100 Å thick. On crystallisation in the elctron beam, thinner portions of the film (which were still in post-nucleation stage) assumed random orientations, whereas thicker portions (where the film had become electrically continuous) took up a single crystalline orientation.

3.2 Mica Substrates

The results of the electron microscope study on thin films of antimony evaporated onto air-cleaved mica substrates are analogous to the ones for *KCl* substrates, except for one small difference. It has been observed that in the case of films obtained by evaporation of antimony onto mica

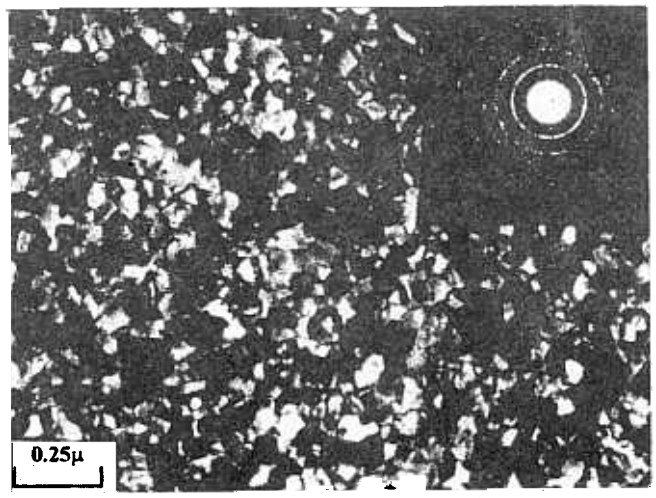

Figure 6. Antimony film (500 Å thick) deposited onto mica substrate at 250 °C and at a rate of deposition 20 Å/s.

and *KCl* substrates maintained at the same elevated temperature and grown in otherwise identical conditions, the grain size in film grown on mica is larger than the grain size in corresponding film grown on *KCl*. Figure 6 shows an antimony film 500 Å thick grown on mica substrate at 250 °C and at a rate of deposition ~ 20 Å/s.

3.3 Amorphous Carbon Substrates

3.3.1 *Room Temperature Substrates*

Figures 7(a) and 8(a) are typical electron micrographs of films grown on amorphous carbon substrates at room temperature and at a low rate of evaporation (~ 20 Å/s). Figure 7(a) shows an antimony film ~ 100 Å thick in the post-nucleation stage, while Fig. 8(a) shows the micrograph of an eletrically continuous film 250 Å thick. SAD patterns in the inset show that the films are amorphous. Increase in the rate of evaporation does not affect the structure of the films either in the post-nucleation stage or when the films have attained electrical continuity (although still in the channel stage).

3.3.2 *High Temperature Substrates*

If the temperature of the amorphous carbon substrate is > 100 °C, films obtained are crystalline, both at low as well as at high rates of evaporation, extending in range from ~ 10 Å/s to ~ 200 Å/s. Films in the post-nucleation stage as well as electrically continuous films are polycrystalline in this case.

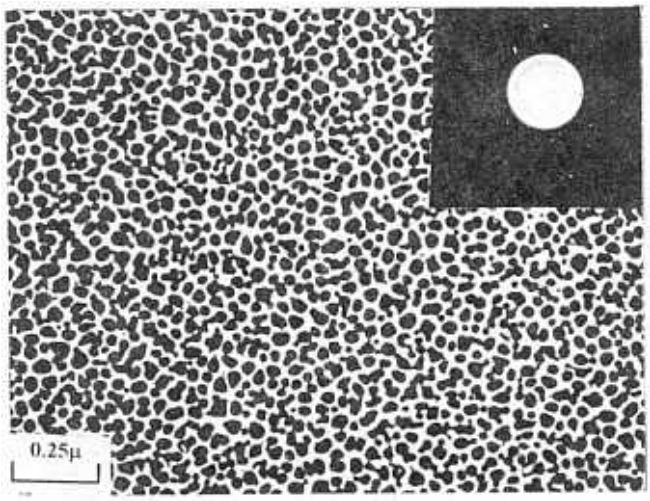

Figure 7(a). Antimony film (100 Å thick) deposited onto amorphous carbon film at room temperature and at a rate of deposition 20 Å/s.

Figure 9 shows an electron micrograph of an antimony film 250 Å thick prepared by evaporation on the amorphous carbon substrate held at 250 °C, the rate of evaporation being 20 Å/s.

3.3.3 *Electron Beam Irradiation*

As in the case of films prepared on *KCl* substrates, amorphous films prepared on amorphous carbon substrates at room temperature are amorphous and crystallise readily in the electron beam of moderate intensity. The films in the post-nucleation stage assume random orientation, while electrically continuous films take up single crystalline orientation

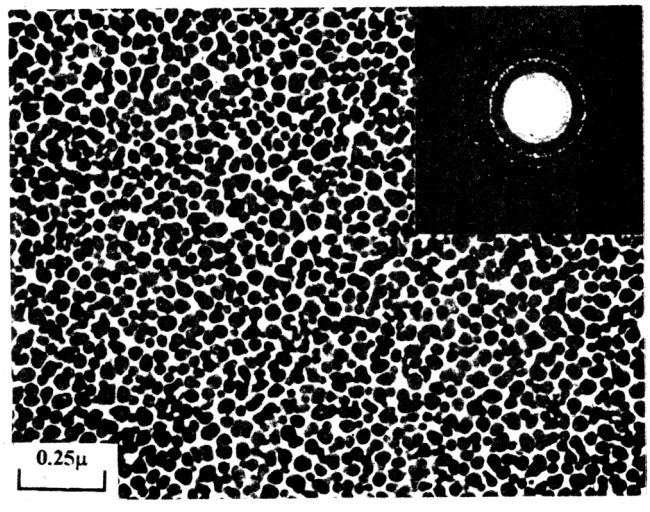

Figure 7(b). Antimony film of Fig. 7(a) after exposure to an electron beam of moderate intensity inside the electron microscope.

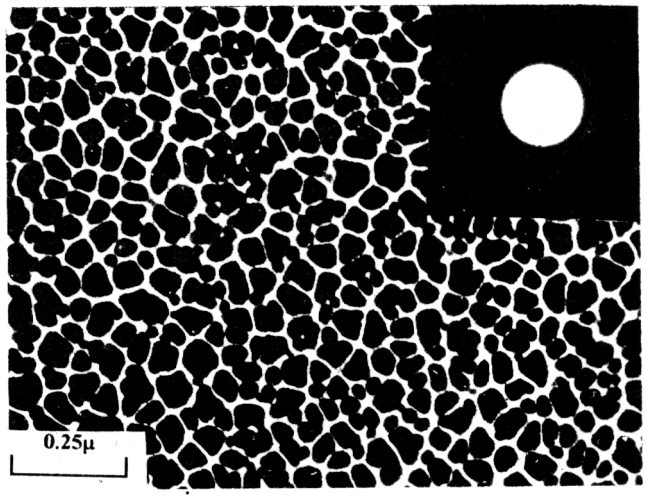

Figure 8(a). Antimony film (250 Å thick) deposited onto amorphous carbon film at room temperature and at a rate of deposition 20 Å/s.

on crystallisation in the electron beam. After crystallisation, the continuous films have been found to have their (111) parallel to the deposit surface. Figures 7(b) and 8(b) show the electron micrographs of the films as shown in Figs 7(a) and 8(a) respectively, after irradiation in the electron beam.

3.4 Highly-Doped *KCl* Substrates

The studies of antimony films obtained by evaporation on doped *KCl* substrates were conducted to investigate the role of dopant on nucleation and growth processes. In these investigations, *KCl* crystals doped with strontium (2 per cent) were used as the

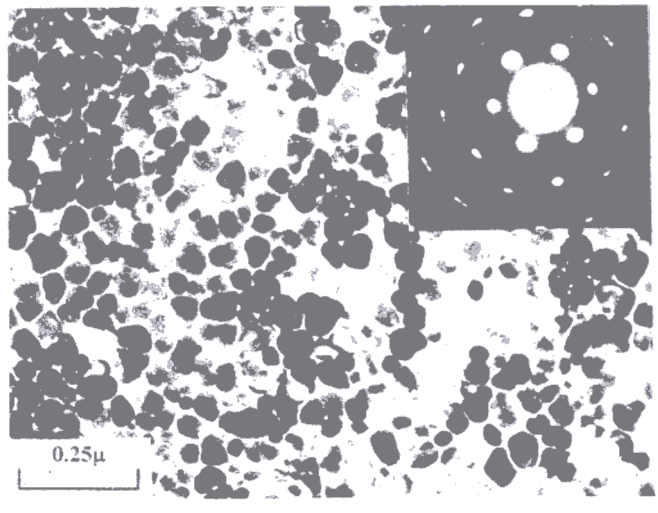

Figure 8(b). Antimony film of Fig. 8(a) after exposure to an electron beam of moderate intensity inside the electron microscope.

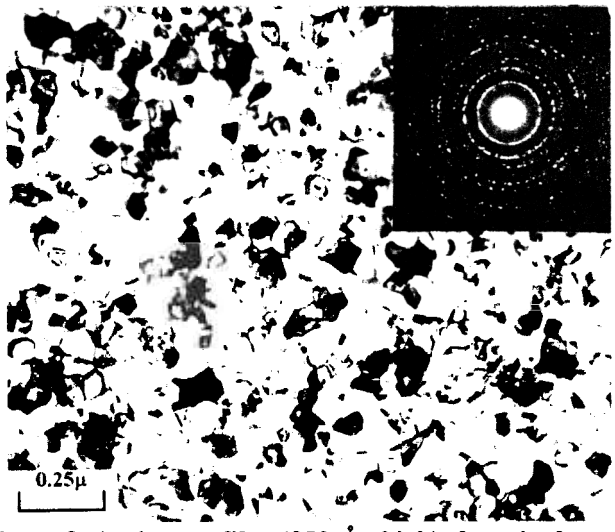

Figure 9. Antimony film (250 Å thick) deposited onto amorphous carbon film at 250 °C and at a rate of deposition 20 Å/s.

substrates. Comparative studies of evaporation on doped and undoped crystals were conducted under identical conditions.

Figures 10(a) and 10(b) show the initial stages of nucleation on undoped and doped crystals of *KCl* (placed side by side in the evaporation chamber), respectively. The evaporation was done onto substrates held at room temperature at a rate of deposition ~10 Å/s. A comparison of the two micrographs reveals that the nucleation on the dopant sites is preferential. In the case of continuous amorphous

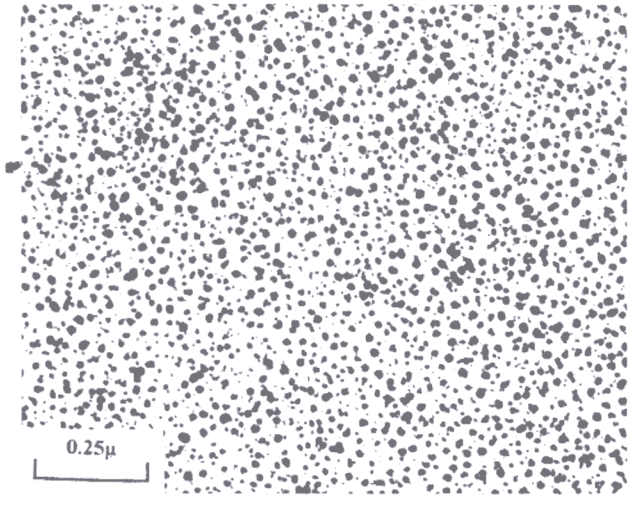

Figure 10(a). Antimony film (~ 50 Å thick) in the nucleation stage, deposited onto *KCl* substrate at room temperature and at a rate of deposition 10 Å/s.

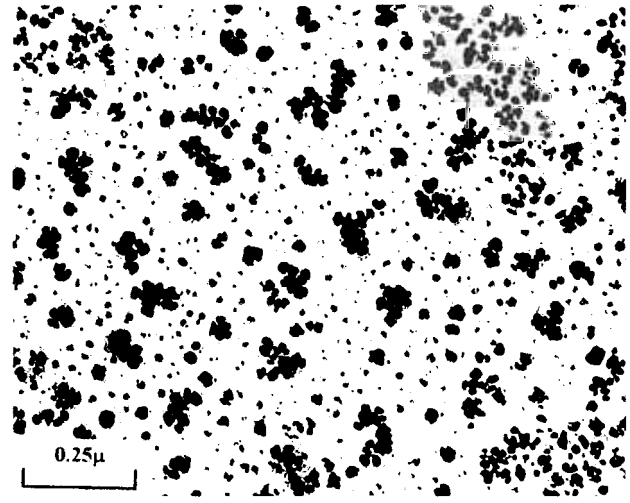

Figure 10(b). Antimony film (~ 50 Å thick) in the nucleation stage, deposited onto doped *KCl* substrate at room temperature and at a rate of deposition 10 Å/s.

films, no change was observed in the microstructure of the films prepared under identical conditions on doped and undoped crystals, either before or after crystallisation, by irradiation in the electron beam.

4. DISCUSSION

Observations show that antimony films evaporated onto room temperature *KCl* substrates have an amorphous structure when examined in a 40 KV-100 KV electron beam at low intensity. As the electron beam intensity is increased (~ 20 μA total current), there is a sudden transformation to the crystalline form. It is further observed that the crystallisation of the films in the post-nucleation stage leads to polycrystalline orientation [Figs 1(a) and 1(b)]. However, when thicker and continuous amorphous films (thickness ~ 250 Å) are crystallised in the electron beam, they always take up a preferred orientation with $(111)_{Sb}$ // $(001)_{KCl}$ [Figs 2(a) and 2(b)]. Varying the rate of deposition seems to have no effect on the crystallisation or orientation of the crystallised films.

If the substrate temperature is >100 °C, films grown on all substrates are crystalline in nature. If the rate of evaporation is kept low (~10 Å/s), films in the nucleation stage as well as continuous films are polycrystalline in nature (Figs 3 and 4). However, if the rate of evaporation is high (>100 Å/s), continuous films have a preferred orientation (Fig. 5), whereas films in the nucleation

stage remain polycrystalline

As in the case of films grown on *KCl* substrates, the films formed on amorphous carbon substrates at room temperature are found to be amorphous at both slow and high rates of evaporation. Similarly, when these amorphous films are exposed to an electron beam of moderate intensity, they crystallise. The films in the nucleation stage assume random orientation, while the continuous films take up a single crystalline orientation on crystallisation, with $(111)_{Sb}$ parallel to the deposit surface. However, if the substrate temperature is high (200 °C), films obtained are polycrystalline at both slow and high rates of evaporation.

These results can be explained on the hypothesis that all these films grow in the amorphous phase initially and crystallise subsequently, either on annealing or on exposure to the electron beam. At high substrate temperatures and low rates of deposition, the transformation to the crystalline form occurs when the deposit is still in the post-nucleation stage, with nuclei assuming random orientation on crystallisation. Further deposition, therefore, results in a polycrystalline film. This is probably due to the fact that at low rates of deposition, the number of nuclei of condensation generated per unit area of the substrate is relatively small, so that coalescence of the crystallised nuclei takes place at a later stage in film growth, resulting in a polycrystalline film.

If the rate of evaporation is high, the transformation to the crystalline state occurs in the nucleation stage in this case also. But because of higher rate of deposition, the number of nuclei of condensation per unit area is large and, therefore, the coalescence of nuclei takes place at an early stage in film growth and the film takes up a single crystalline orientation as suggested by Matthews[9].

It is further seen that in the case of evaporation onto amorphous substrates maintained at high temperature, the films obtained are invariably polycrystalline, even when the rates of evaporation are high. The explanation for results is that in the case of amorphous substrates, it may be difficult for any orientation change of nuclei of condensation to take place at the time of coalescence, due to the lack of mobility of nuclei on amorphous substrates

5. CONCLUSIONS

TEM and elctron diffraction studies of evaporated thin films of antimony show that antimony films evaporated onto room temperature *KCl* and amorphous carbon substrates have an amorphous structure when examined in a 40 KV-100 KV electron beam of moderate intensity. As the electron beam intensity is increased (~ 20 μA total current), there is sudden transformation to the crystalline form. Crystallisation of films in the post-nucleation stage leads to polycrystalline orientation, while thicker and continuous amorphous films crystallise to take up the orientation $(111)_{Sb}$ // $(001)_{KCl}$. If the substrate temperature is > 100 °C, films grown on all substrates are crystalline in nature. If the rate of deposition is high (~100 Å/s), the films in the nucleation stage are polycrystalline, while continuous films have a single crystalline orientation. On doped crystals of *KCl*, nucleation is preferential on impurity sites.

From these results, it is concluded that as in the case[10] of *CdSe*, thin films of antimony prepared by effusion from the Knudsen-type source compare well with those prepared by other conventional sources of vacuum evaporation.

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