CHEMICAL VAPOR TRANSPORT IN RF HYDROGEN PLASMA

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ABSTRACT

Thin films of Se, Te and Se-Te were prepared on a suitable substrate by transport of those substances in rf glow discharge of hydrogen at a low pessure. These films were crystalline and deposited only outside the discharge. The transport of boron was possible only in rf arc discharge of hydrogen at low pressures. Boron film has not been obtained yet in glow discharge of hydrogen.

1. INTRODUCTION

A number of studies have been carried out on the heterogeneous reactions in low pressure plasmas as reviewed by Veprek(1). Ing and Chiang(2)found out that the deposition of thin films of Se, As and Te was possible by chemical transport of these substances in a low pressure hydrogen plasma. The success of such plasma transport processes suggests the formation of some volatile hydrides which are thermodynamically stable in the presence of the plasma but not in its absence. Veprek and his coworkers(1) reported that C, Ge, Si and P were transported with hydrogen plasma.
In this study, as the first step, the preparation of thin films of Se, Te and Se-Te was attempted by the plasma transport process in a vertical quartz reactor including rf induced hydrogen glow discharge at low pressures and the characteristics of these films were investigated by AES, TEM, SEM and X-ray diffraction analysis, attaching importance to the microstructure. Then, as the second step, the plasma transport of boron was examined in rf glow and arc discharges of hydrogen and the characteristics of deposited film were investigated by the same methods as applied to chalcogen films described above.

2. EXPERIMENTAL

The schematic diagram of the experimental apparatus used for the preparation of Se, Te and Se-Te films is shown in Fig.1. The rf(4MHz) hydrogen plasma was generated in a water-cooled quartz tube of inner diameter 45mm with 3 turns of rf coil made by copper tube. The quartz tube is connected to a stainless chamber, in which a brass substrate holder with twelve deposition plates arranged spirally at intervals of 1 cm as shown in Fig.1, rotates at about 5 rpm. A hole, 5mm in diameter and 2mm in depth, was bored in each plate and the mesh grid carrying Colloidion film for TEM was placed in each hole. About 1g of Se(99.99%) and/or Te(99.99%) shots(2-3mmϕ) were set in a quartz basket.
The experimental apparatus for the plasma transport of B is illustrated in Fig.2. In the preliminary experiment, a graphite substrate was placed just under the quartz tube with three turns of coil and an alumel -chromel thermocouple was inserted into the substrate to measure gas temperature inside and outside the hydrogen plasma. In the main experiment, crystalline(β-

rhombohedral boron granules were hung by fine tugsten wires in the quartz tube. A silicon wafer(100) were used as the substrate in most cases, but a stainless steel plate or a NaCl crystal was used in some cases. The substrate was placed on a quartz pedestal and the substrate temperautre was monitored by the alumel-chromel thermocouple.

3. RESULTS AND DISCUSSIONS

3-1. Deposition of thin films of Se, Te and Se-Te

The quartz bascket containing the sample was fixed at 1.5cm below the lowest end of the rf coil. The quartz tube and the stainless steel chamber were evacuated to 6×10^{-2} Torr by a rotary vacuum pump, then the pressure was maintained at 0.5 Torr under hydrogen gas flow of 90-115$cm^3\cdot min^{-1}$. The plate input power of the rf power generator was 3KVx0.52-0.58A and the reaction time was 0.5 and 2hrs. The temperature of Se or Te or Se-Te source and the substrate temperature were maintained at 340-350K and 290-300K respectively. The relation between the substrate position, that is, its distance L from the lowest end of the coil and the appearance of depoist on the substrate (the mesh grid) observed by TEM is summarized in fig.3.. The lower region of hydrogen glow discharge reached to L=12.5cm. This fact suggests that the deposition does not occur in the plasma region.

Fig. 4 shows an example of the microphotographs of Se deposited at L=21cm for 30min. The electron diffraction patterns revealed that these islands of deposited Se were crytalline. The shape of each Te island was somewhat different from that of Se. The log-probability plots showing the relation between the island's size and its cumulative percentage are illustrated in Fig.5. The standard deviation values were estimated to be 1.38 and 1.36 for Se and Te respectively. It can be concluded from these results that the nucleation and growth of Se and Te crystals occur on the substrate surface.

Fig. 6 shows the microphotograph of Se-Te film deposited at L=21cm for 2 hrs. In this case, the same quantities of Se and Te were placed in the quartz basket. The composition of Se-Te alloy film was estimated to be $Se_{26}Te_{74}$ by the lattice parameter of the alloy determined by X-ray diffraction analysis.

There still remains several problems to be made clear about such plasma transport at low temperature. The first one is to identify chemical species such as volatile hydride radicals which may be generated from the source substance in hydrogen discharge. The second one is to explain more quantitatively the theoretical basis of such plasma transport. The third one is to investigate whether the deposition rate, the structure, the composition and other properties can be controlled.

3-2. Deposition of thin film of boron

In the first transport experiment, the source of only one boron granule, was placed in hydrogen glow discharge at a pressure of 1 Torr and heated to 478-823K, but the transport of boron was not observed. In the second transport experiment, the boron sample was placed on a graphite substrate heated inductively to 1473-1573K with hydrogen glow discharge at a pressure of 10 Torr for 10-60min. and the formation of some deposit was observed. The color of such deposit was white in most cases. Blue-black deposit was also obtained but its color changed to white in an air atmosphere. This white deposit seemed to be boron oxide. In the third transport experiment, the source of many boron granules as shown in Fig.2, was heated in hydrogen arc discharge at 1 Torr and a higher power input. The deposit was obtained on a Si substrate in 30-60min.. B,Si,O,N and C were detected by AES of the deposit. Considering these results, it was decided to carry out the following transport experiments of boron in hydrogen arc discharge at low pressures. before the fourth experiment, the substrate temperature was determined by

alumel-chromel thermocouple and related to the pressure and the input power in hydrogen discharge. Fig.7. shows the relation between the substrate temperature and its position (the distance from the lowest end of rf coil). The increase of the input power resulted in the shift from glow discharge to arc discharge easily. The temperature inside the quartz tube at the coil position was too high at 1 Torr and 3-4KV (plate voltage of rf power generator) for boron source. Therefore, the transport experiment was performed at 0.5 Torr and 3.5KV x 1.4A. It was estimated that the temperature of boron source reached to 1500-1700K under these conditions.

The presence of carbon and oxygen was confirmed by AES of the surface of Si wafer substrate without hydrifluoric acid etching as a pretreatment. But these impurities were completely removed by 10min ion etching. The surface of boron source was contaminated with carbon and oxygen.

After the transport experiment of boron, a very thin film with light brown color was found on the inner wall of the quartz tube near the rf coil region. Fig.8. is an example of photographs by SEM of the film formed on the Si substrate at T_S=723K (substrate temperature) during 30min transport. Such aspect of the film showed a variety, depending on its position on the substrate and the deposition time. Fig.9. shows Auger spectra of the film deposited for 2 hrs at T_S692K. Si,C,N and O were detected as main impurities with boron. The inner wall of the quartz tube exposed to hydrogen arc discharge may be an origin of Si in the film. The Auger spectra of boron nitride is similar to those of the deposited film. It must be clarified whether the reaction between the boron film and nitrogen proceeds easily.

The substrate temperature was controlled from 457K to 852K by putting the substrate closer to the plasma region. The composition or the concentration ratio of each component of the film was about constant in it except the surface layer removed by 10 min. ion etching. The increase of Si concentration was observed by putting the substrate at a high temperature region. The atomic ratio of B/Si in the film increased remarkably by maintaining the substrate temperature lower than 673K. The highest ratio was about 2. As a trial, the film deposited on a copper mesh was investigated by AES. The concentration of each impurity except silicon was negligible in this case. The copper mesh seems to work as a kind of impurities getter. Fig.10. is a photograph obtained by SEM of the film deposited on the copper mesh during 30 min. transport. It can be estimated from this figure that the growth rate of the film was about 300A·min^{-1}. In a 3hrs experiment at 0.5 Torr and 3.5KV x 1.4A, this growth rate was about 500A·min^{-1}. The electron diffraction analysis of the film deposited on a NaCl substrate revealed that the most part of the film was amorphous, but very small crystalline parts were detected in some cases. The growth rate of the film on the NaCl substrate was smaller than that on Si substrate.

The film deposited on Si substrate during 6 hrs transport was heated for 3 hrs at 1273K. The change of the surface structure during the heating was confirmed by SEM. Tetragonal boron phase may appear from the amorphous film, which can be estimated from the X-ray diffraction analysis. But the broadening of the diffraction lines remained after the heat-treatment, and the change of film structure from "amorphous" to "crystalline" was on the way.

The equilibrium partial pressures of various boron hydrides such as BH, BH_2 and BH_3, even if they are present, are calculated to be 10^{-7} atm at most between 1500 and 1700K, because the temperature of the boron source is estimated to be between these temperatures. This means that the mass loss from the boron source is too low to prepare the boron film in such temperature range.

The transport of boron was tried for 30 min. in Ar arc discharge at 0.5 Torr and 3.5KV x 1.4A. The film deposited on a stainless steel substrate, but boron was not detected by AES of the film. Such result is considered to be

one proof that the transport of boron is not due to sputtering. Si,C,O,Fe and Cr were detected in this film. The fact that silicon is transported suggests the possibility of sputtering on the inner surface of the quartz tube.

CONCLUSIONS

1. Se,Te and Se-Te films deposited on the substrate kept at room temperature by the transport from those substances placed in hydrogen glow discharge.
2. The film deposition did not occur in the glow discharge region.
3. The films were crystalline. It is considered that larger cooling velocity is necessary to obtain amorphous film.
4. B can be transported from the boron source placed in low pressure hydrogen arc discharge to the substrate kept at a low temperature under the discharge.
5. The deposited film was amorphous and the deposition rate was $500A \cdot min^{-1}$.
6. Si,C,N and O were included as impurities in the film.
7. The transport of B is considered to be impossible under the equilibrium condition of B-H_2 system at temperatures in the experiments.
8. The chemical species originated from B in the discharge must be identified by the suitable analytical means such as mass spectrometry, and the mechanism of such plasma transport must be clarified.

REFERENCES

(1) S.Veprek, "Current Topics in Materials Science", Vol.4. edited by E.Kaldis (North-Holland Publishing Company,1980), Chap.4
(2) S.W.Ing,Jr., and Y.S.Chiang, J.Electrochem.Soc., 113, 192(1966)

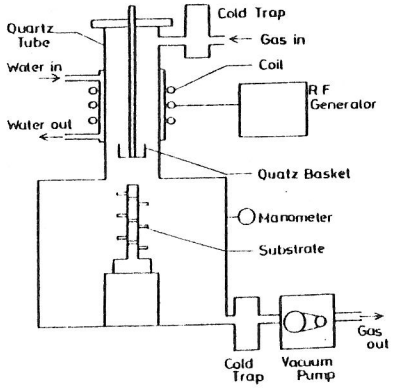

Fig.1. Experimental apparatus for deposition of Se, Te and Se-Te films.

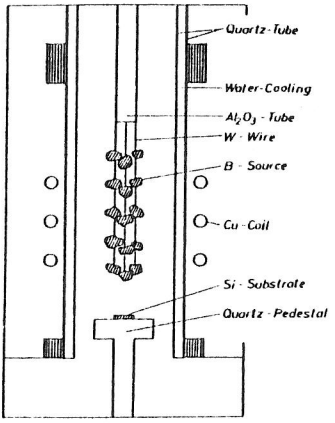

Fig.2. Experimental apparatus for deposition of boron film

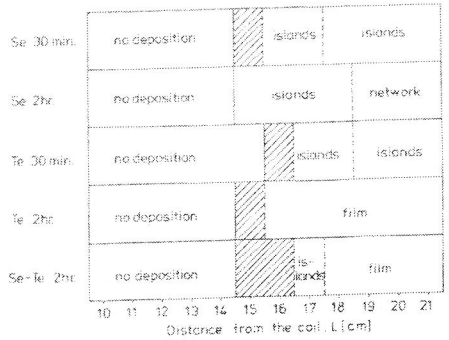

Fig.3. The relation between the appearance of the deposit and the substrate position (distance from rf coil)

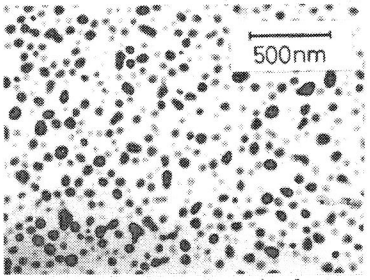

Fig.4. TEM of Se deposited at the distance from rf coil of 21cm (30min.)

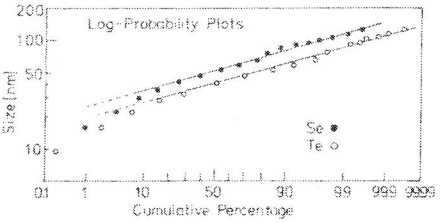

Fig.5. Log-probability plots based on the results of TEM.

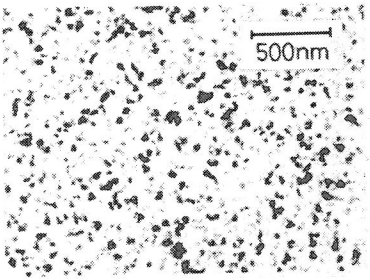

Fig.6. TEM of Se-Te film deposited at the distance from rf coil of 21cm (2 hrs.)

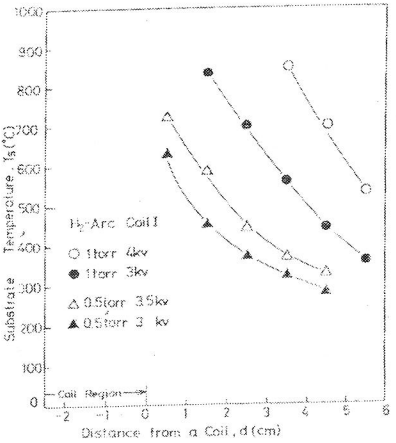

Fig.7. The relation between the substrate temperature and its distance from rf coil

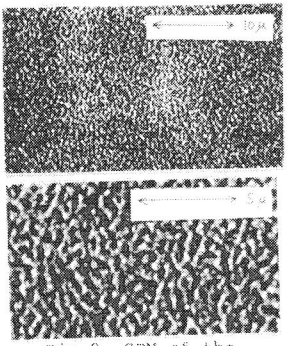

Fig.8. SEM of the deposited film, $T_s = 723$ K (30 min.)

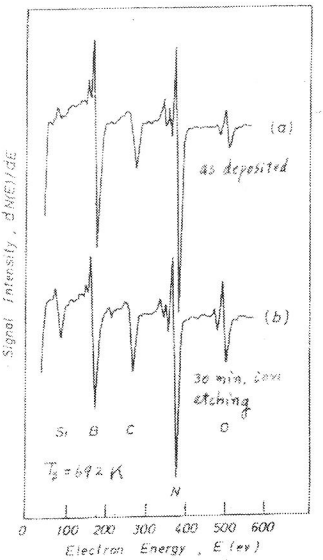

Fig.9. Auger spectrum of the deposited film (2 hrs.)

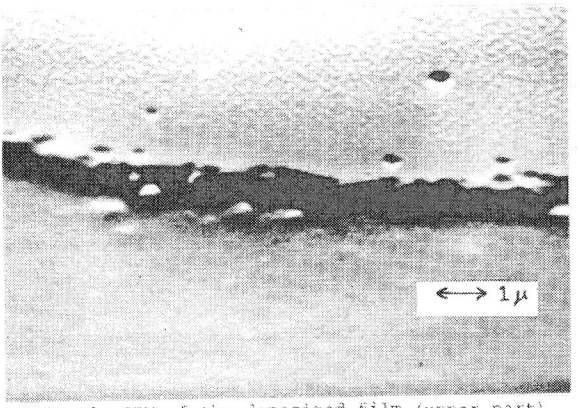

Fig.10. SEM of the deposited film (upper part) on Cu mesh. $T_s = 591$ K (30 min.)