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PREPARATION OF SiC FILMS BY PHOTOCHEMICAL VAPOUR DEPOSITION USING A D₂ LAMP

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Abstract—SiC films have been prepared by photochemical vapour deposition using a D₂ lamp from a gas mixture of CH₃SiCl₃+H₂+Ar on a graphite plate. The deposition temperature of the SiC films of a single phase was lowered by irradiation with a D₂ lamp by 50°C as compared to that without irradiation. Furthermore, the deposition rate was increased with irradiation by 1.2–2.8 times as compared to that without irradiation.

1.—Introduction

Chemical vapour deposition (CVD) is a very important process for obtaining adherent protective coatings against oxidation, corrosion or abrasion, electrical conducting or insulating films, optical films, diffusion barriers, etc. However, the CVD process has many significant shortcomings, such as a limited number of materials for substrates or apparatus, degradation of the strength of the substrate, grain growth, etc. These shortcomings are mainly due to high-temperature processing. Accordingly, many low-temperature processes such as plasma CVD, organometallic CVD, photo CVD, catalytic CVD (1) are now being actively investigated to overcome these shortcomings. These low-temperature CVD processes are mainly used in semiconductor technology, but rarely used in the engineering fields. Preparation of the films of Si (2–4), SiO₂ (5,6), Si₃N₄ (6,7), AlN (8), TiB₂ (9) etc. has been demonstrated using photo-CVD with a low-pressure Hg lamp, laser or D₂ lamp.

2 Recently, we have obtained thin films of TiC (10), TiN (11) and TiB₂ (12) on stainless steels or graphite plates by photo-CVD process using a D₂ lamp. We have found that the deposition temperature of these films were lowered by irradiation with the D₂ lamp by 50–150°C as compared to that without irradiation. Furthermore, we have found that the deposition rates were increased by 35–300% with irradiation.

In this work, we have obtained the SiC films on graphite substrates by a photo-CVD process using a D₂ lamp from a gas mixture of methyltrichlorosilane and hydrogen. The effects of irradiation by the D₂ lamp on the deposition temperature and deposition rate of the SiC films of a single phase were examined in some detail.

2.-Experimental procedure

Experimental apparatus used in this work is schematically shown in Fig.1. The substrate (graphite plate, 12x18x1 mm³) was polished using emery paper (No. 800), degreased ultrasonically, dried, and set vertically in the horizontal reaction tube (quartz, 24 mm i.d. x 300 mm long). Vacuum ultraviolet light (200 nm) from a D₂ lamp (Hamamatsu Photonics, L1314, 150 W) was directed through a window of a synthetic quartz glass (1 mm thick) onto the substrate. The distance from the D₂ lamp to the substrate was fixed at 130 mm. Methyltrichlorosilane (MTS) saturated in the hydrogen carrier gas using a circulation-type saturator and introduced into the reaction zone.

3.-Results and Discussion

X-ray diffraction patterns of the surface of the deposits obtained at various reaction temperatures with and without irradiation by the D₂ lamp are shown in Fig.2. It can be seen that, without irradiation by the D₂ lamp, free Si was codeposited with SiC phase in a temperature range of 1000-1050°C, and that the SiC films of a single phase were obtained at a temperature as high as 1100°C. On the other hand, it can be seen that, with irradiation by the D₂ lamp, SiC films of a single phase without codeposition of free Si were obtained at a temperature as low as 1050°C. This temperature is 50°C lower than that without irradiation. Similar lowering of the deposition temperature with irradiation by the D₂ lamp has been reported for the deposition of TiN films from a gas mixture of TiCl₄-NH₃-H₂-Ar (11).

The effect of the reaction temperature on the weight gain of the deposits for 30 min reaction time is shown in Fig.3, in which the open circle and open triangle denote the deposition of the SiC films of a single phase, while solid ones denote that of a mixed phase of SiC and a free Si. The weight gain of the deposits with irradiation by the D₂ lamp was always larger than that without irradiation, and was about 2.2 times at 1000°C and 1.2-1.3 times at 1050-1100°C. It is important to know whether or not this weight increase with irradiation by the D₂ lamp was affected by the increased deposition rate of free carbon. It was reported that deposition rate of the TiC films from a gas mixture of TiCl₄+CH₄ (or CCl₄)+H₂+Ar was increased by irradiation from a D₂ lamp by 1.5-2.2 times as compared to that without irradiation, and that deposition of a free carbon was not observed with irradiation (10). Accordingly, it may be considered that the increase in the weight of the deposits with irradiation was effected not by the increased deposition of free carbon but by deposition of a SiC single phase.

X-ray diffraction profiles of the deposits obtained at various gas flow rates of MTS are shown in Fig.4, in which the reaction temperature was fixed at 1050°C. Without irradiation by the D₂ lamp, the mixed phase of SiC and free Si was always deposited at all gas flow rates of MTS used in this work. On the other hand, with irradiation by the D₂ lamp, the SiC films of a single phase were always deposited. At a reaction temperature of 1100°C,

the SiC films of a single phase were deposited with and without irradiation at all gas flow rates. That is, an irradiation effect of the D_2 lamp on the deposition of the SiC films of a single phase was observed at a relatively low temperature of 1050°C .

The effect of the gas flow rate of MTS on the weight gain of the deposits is shown in Figs. 5 and 6, in which reaction time was fixed at 30 min. It can be seen that the weight gain with irradiation by the D_2 lamp was increased by increasing the gas flow rate of MTS and was always 1.3-1.6 times as compared to that without irradiation at temperatures of 1050°C and 1100°C .

The effect of reaction time on the weight gain of the deposits is shown in Fig. 7, in which reaction temperature was fixed at 1100°C . The weight gain with irradiation was always larger than that without irradiation, and was 2.5-2.8 times as compared to that without irradiation at an initial deposition stage of 10-20 min reaction time. This result suggests that irradiation by the D_2 lamp accelerates the formation of nuclei of a SiC phase especially at the initial stage of deposition. A similar effect of accelerated formation of nuclei was observed for TiB_2 films obtained from a gas mixture of $\text{TiCl}_4 + \text{BCl}_3 + \text{H}_2 + \text{Ar}$ (12).

Vacuum ultraviolet light (200 nm) was directed vertically onto the substrate through a stream of a source gas ($\text{MTS} + \text{H}_2$) as shown in Fig. 1. Accordingly, the following activated processes may be expected. 1) A source gas (MTS) in a vapour phase is activated by irradiation with the D_2 lamp to form activated molecules, radicals, fragments, etc. 2) Si species, which are formed by the decomposition of MTS and adsorbed on the surface of the substrate are activated, and these activated Si species readily react with carbon species to form SiC species at relatively low temperature. Accordingly, deposition of free carbon may be suppressed. 3) Molecules or fragments adsorbed on the surface of the substrate are activated, and the surface reaction is accelerated. Accordingly, supersaturation on the surface of the substrate is increased to form many nuclei. 4) Some surface energy is added on the surface of the substrate to activate the nucleation of a SiC phase. It may be suggested that the lowering of the deposition temperature of the SiC films of a single phase is mainly effected by the irradiation effects of 1) and 2), and the increasing of the deposition rate by the effects of 3) and 4).

4.- Conclusions

SiC films have been prepared by photo CVD using a D_2 lamp from a gas mixture of $\text{CH}_3\text{SiCl}_3 + \text{H}_2 + \text{Ar}$ on a graphite plate. The deposition temperature of the SiC films of a single phase could be lowered by irradiation from a D_2 lamp by 50°C as compared to that without irradiation. Furthermore, the deposition rate could be increased by 1.2-2.8 times as compared to that without irradiation.

5.-References

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Fig.1. Schematic of the apparatus.

a) D_2 lamp, b) H_2 or Ar, c) substrate (graphite plate), d) electric furnace, e) reaction tube (quartz), f) gas outlet, g) CA thermocouple, h) Ar, i) H_2 , j) saturator of CH_3SiCl_3 , k) oil bath.

Fig.2. X-ray diffraction patterns of the surface of the deposits (Effect of reaction temperature). (a)-(c): Without irradiation by a D_2 lamp, (d)-(e): with irradiation. Reaction temperature: (a) 1000°C , (b) 1050°C , (c) 1100°C , (d) 1000°C , (e) 1050°C . CH_3SiCl_3 gas flow rate = 0.16 cc/s , H_2 flow rate = 2.0 cc/s , Ar flow rate = 3.0 cc/s . (○): $\beta\text{-SiC}$, (△): Si. Other peaks denote the graphite substrates.

Fig.3. Effect of reaction temperature on the weight gain of the deposits. CH_3SiCl_3 gas flow rate = 0.16 cc/s . Reaction time = 30 min. (△) and (▲): Without irradiation by a D_2 lamp, (○) and (●): with irradiation. (●) and (▲): $\beta\text{-SiC}+\text{Si}$, (○) and (△): $\beta\text{-SiC}$ single phase.

Fig.4. X-ray diffraction patterns of the surface of the deposits (Effect of gas flow rate of CH_3SiCl_3). Reaction temperature: 1050°C . CH_3SiCl_3 gas flow rate=(a) 0.08 cc/s, (b) 0.16 cc/s, (c) 0.32 cc/s, (d) 0.08 cc/s, (e) 0.16 cc/s, (f) 0.32 cc/s. (a)-(c): Without irradiation by a D_2 lamp, (d)-(f): with irradiation. (○): β -SiC, (▲): Si. Other peaks denote the graphite substrate.

Fig.5. Effect of gas flow rate of CH_3SiCl_3 on the weight gain of the deposits. Reaction temperature= 1050°C , reaction time=30 min. (▲): Without irradiation by a D_2 lamp, (○): with irradiation. (▲): β -SiC+Si, (○): β -SiC single phase.

Fig.6. Effect of gas flow rate of CH_3SiCl_3 on the weight gain of the deposits.

Reaction temperature=1100°C, reaction time=30 min. (Δ): Without irradiation by a D_2 lamp, ($\circ$): with irradiation. ($\circ$) and (Δ): β -SiC single phase.

Fig.7. effect of reaction time on the weight gain of the deposits.

Reaction temperature=1100°C, reaction time=30 min, CH_3SiCl_3 gas flow rate=0.24 cc/s. (Δ): Without irradiation by a D_2 lamp, ($\circ$): with irradiation. ($\circ$) and (Δ): β -SiC single phase.