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Effect of substrates on morphological evolution of a film in the silicon CVD process: approach by charged cluster model

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Abstract

Film morphology depends on the types of substrates used in the CVD process. This dependency has been studied based on the charged cluster model in the silicon CVD process. There exists a strong correlation between microstructure evolution and the charge transfer rate (CTR) of substrate materials. Films tended to be porous on substrates with a high CTR and dense on substrates with low CTR. The microstructure evolution could be explained by the interaction of charged clusters with the substrate. On substrates with a high CTR, charged clusters lose their charge quickly prior to landing. The resultant neutral clusters undergo attraction-dominant random sticking (flocculation), leading to a porous structure. On substrates with a low CTR, charged clusters lose their charge slowly after landing and undergo repulsion-dominant selective sticking (deflocculation), leading to a dense film. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In the chemical vapor deposition (CVD) process, the deposition behavior depends on the type of substrate. Deposition on conducting substrates is much more favorable than on insulating ones. This fact has been utilized for selective deposition in the CVD process [1]. Recently, we compared the deposition behavior between conducting and insulating substrates in the silicon CVD process [2]. On conducting substrates, the deposition of silicon continued with processing time at a relatively high rate. On insulating substrates, however, some silicon particles deposited in the initial stage and then etched away at the later stage. The same phenomenon was reported earlier by Kumomi et al. [3,4].

This puzzling phenomenon could be successfully explained by assuming gas-phase nucleation and

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subsequent deposition of those nuclei based on the phase diagram in the Si–Cl–H system [2,5]. The charged cluster model (CCM), which was originally suggested as the growth mechanism for diamond CVD [6,7], was also shown to apply to the silicon CVD process. In the CCM, charged clusters of a few nanometers are formed in the gas phase and they become the building block. The existence of hypothetical charged clusters was experimentally confirmed in diamond CVD [8], silicon [9], and evaporation coatings of gold [10] and tungsten [11].

According to the CCM, the dependence of the deposition behavior on substrates originates from charge. Charged clusters have difficulty in landing on insulating substrates due to Coulomb repulsion while they land easily on conducting substrates. However, the film morphology differs even among some conducting substrates. In the diamond CVD process, porous skeletal graphic soot is evolved on some transition metals such as Fe, Ni and Co while a dense crystalline diamond film is evolved on other substrates such Au, Cu, Mo, W and Si [6]. The CCM suggested that this abrupt change in microstructure evolution among conducting substrates is related to the charge transfer rate (CTR) of the particular substrate materials. The CTR, which corresponds to the hydrogen evolution rate of electrodes used in the electrochemistry, decreases in the order of Pd, Pt, Rh, Ir, Ni, Fe, Au, W, Ag, Nb, Mo, Cu, Ta, Al and Ti [12]. There exists an almost perfect correlation between the film morphology and the CTR of the substrate materials: Pd, Pt, Rh, Ir, Ni and Fe produced porous soot while Au, W, Ag, Nb, Mo, Cu, Ta, Al and Ti produce dense diamonds [13].

Since the CCM also applies to the silicon CVD process, a similar deposition behavior is expected on these conducting substrates. The purpose of this paper is to study the substrate effect on deposition behavior in the silicon CVD process from a viewpoint of the CCM.

2. Experimental procedures

The silicon CVD reactor is a typical one used for epitaxial growth [14]. An electrical-resistance heater was placed below the substrate to control the substrate temperature. The gas phase and the substrate were also heated by halogen lamp, which was separated from the reactor by a quartz plate. The gas showerhead was 10 mm above the substrate. The gas mixture ratio was $SiH_4:HCl:H_2 = 1:1:98$ with a gas flow rate of 100 standard cubic centimeter per minute (sccm). The deposition was done at a substrate temperature of 1123 K under a pressure of 1333 Pa. The deposition time was varied from 3 to 30 min. The substrates were Pd, Pt, Rh, Ir, Ni, Fe, Cu and Ti in the order of decreasing CTR [12].

In order to check for the similar deposition behavior in the sputter deposition, alumina was deposited by sputtering on Fe and Si substrates with a RF power of 100 W at a substrate temperature of 873 K under a pressure of 2.7 Pa.

3. Results and discussion

In the diamond CVD process, the deposition behavior between Fe and Si substrates was markedly different: porous skeletal soot was observed on Fe and dense crystalline diamond on Si [6]. Since silicon films in the CVD process also grew by charged clusters [2,5,9], Fe and Si substrates could show different behaviors also in the Si CVD process. This prediction was confirmed as shown in Figs. 1(a) and (b). The deposition time was 10 min. Deposits on the Fe substrate are porous while those on the Si substrate are dense. It should be noted that Fig. 1(a) is a plan view and Fig. 1(b) is a cross section view. In Fig. 1(b), the bottom half is the substrate. The film thickness on the Fe substrate (Fig 1(a)), was ~5 mm while that on the Si substrate (Fig. 1(b)) was only ~3 μm. This difference in film growth rate between the two substrates is related to the fact that charged clusters have difficulty in landing on a semi-conducting or insulating substrate, leading to preferential deposition on a conducting substrate over a semi-conducting or insulating one [2]. It should be noted that the silicon substrate, unless specially treated, usually has a thin insulating layer of silicon dioxide.

In order to undertake a more general study on the dependence of film morphology on the CTR of

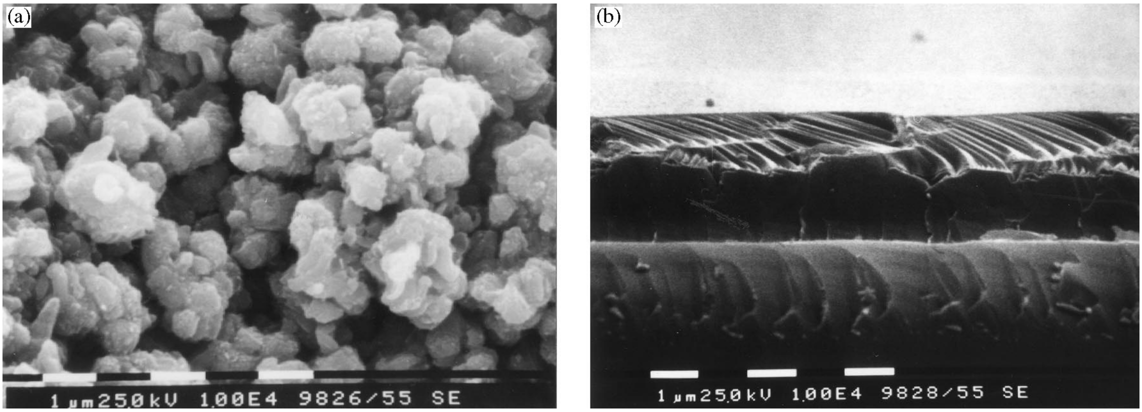

Fig. 1. SEM photographs of silicon deposits on (a) Fe and (b) Si substrates with the $SiH_4:HCl:H_2$ gas ratio of 1 : 1 : 98 under a reactor pressure of 1333 Pa at a substrate temperature of 1123 K.

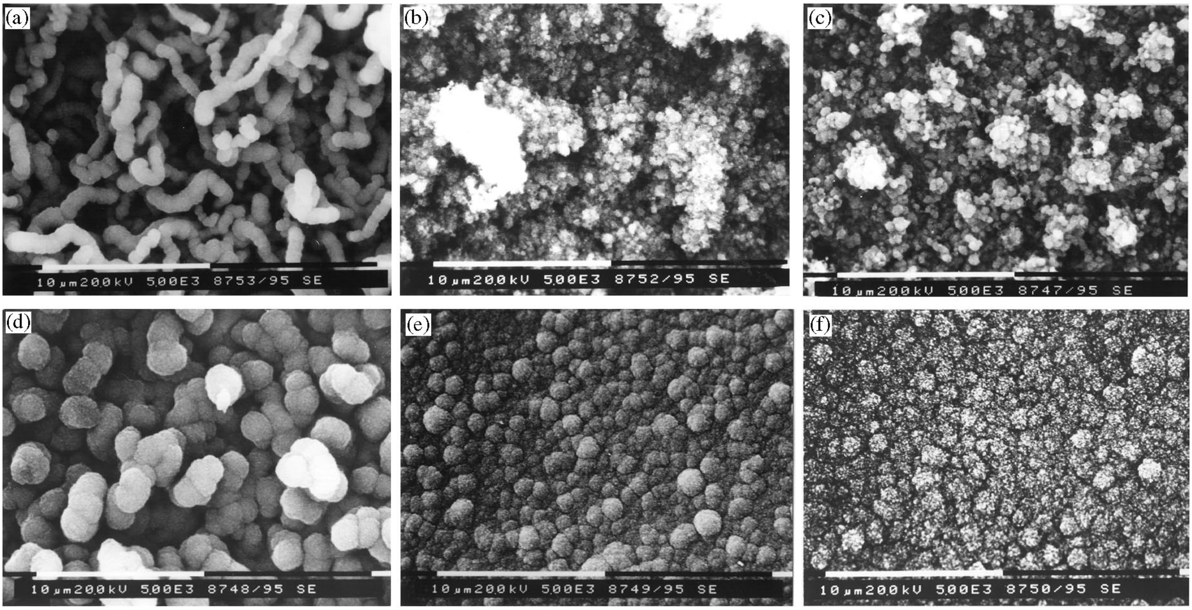

Fig. 2. SEM photographs of silicon deposits on (a) Pd, (b) Rh, (c) Ir, (d) Cu, (e) Cr, and (f) Ti substrates with the same processing conditions as those for Fig. 1.

a particular substrate, the deposition behaviors on six different substrates of Pd, Rh, Ir, Cu, Cr and Ti were compared, as shown in Fig. 2. The deposition conditions were the same as those for Fig. 1. Silicon films on all substrates were approximately 5 mm in thickness with some variations among substrates.

On the Pd substrate (Fig. 2(a)), which has the highest CTR, the microstructure is very porous with cocoon-shaped grains. On the Cu substrate with a medium CTR (Fig. 2(d)), the microstructure is also porous but with ball-shaped grains. Each ball consists of fine grains, resembling a

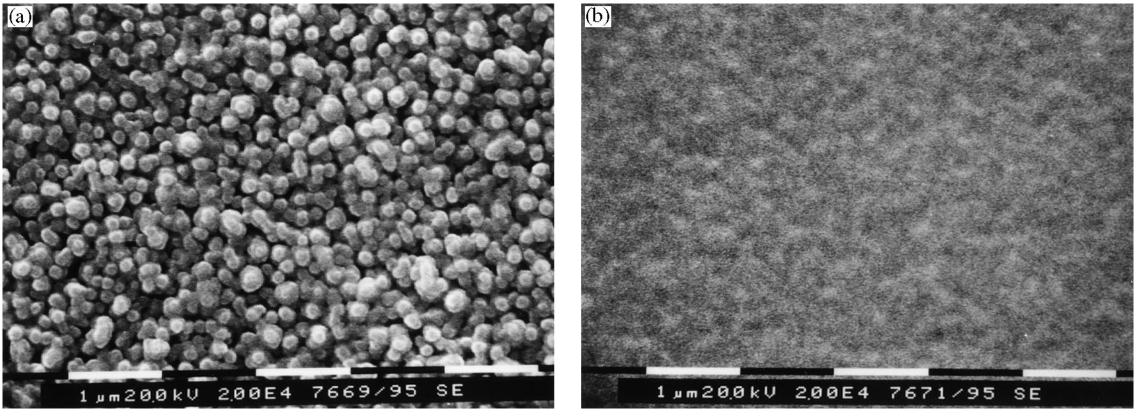

Fig. 3. SEM photographs of sputtered Al_2O_3 films on (a) Fe and (b) Si substrates with a RF power of 100 W at a substrate temperature of 873 K under a reactor pressure of 2.7 Pa.

cauliflower-like structure. On the Ti substrate with the lowest CTR (Fig. 2(f)), the film is dense although the morphology is typical of a cauliflower-like structure. The overall trend is that films become denser with decreasing CTR.

We found out a similar trend in the evaporation coating of W [11] and a ZrO_2 CVD film [15]. In ZrO_2 deposition by laser ablation, we also found that porous and dense films were deposited on Pt and Ti substrates, respectively. In addition, in the sputter deposition of Al_2O_3, porous and dense films were coated on Fe and Si substrates, respectively. The result for Al_2O_3 is shown in Fig. 3 to emphasize the generality of this behavior. The deposition was done at a substrate temperature of 873 K under 2.7 Pa with a RF power of 100 W. Fig. 3(a) shows porous Al_2O_3 deposits on the Fe substrate while Fig. 3(b) shows a dense film on the Si substrate. The tendency for the deposits to be porous on a substrate with a high CTR seems to be general when deposition occurs by charged clusters. This behavior can be an easy criterion to distinguish deposition by charged clusters from atomic unit deposition.

Once the substrate surface is covered, further landing of charged clusters would not be affected by CTR of the substrate. Instead, the CTR of the deposits will affect the deposition behavior. For example, in the CVD diamond process, the porous soot was deposited on Fe in the initial stage but in a later stage diamond crystal grew on the porous soot coating [6,16]. A similar behavior is expected in the deposition of charged Si clusters.

For this, we compared the morphology of silicon films deposited on a Ni substrate between the initial and later stages of deposition, as shown in Figs. 4(a) and (b). The deposition times were 3 and 30 min for Figs. 4(a) and (b), respectively. Fig. 4(a) shows a porous structure with relatively fine grains while Fig. 4(b) shows large grains with well-developed facets on the previously formed fine grains. Fig. 4(b) is very similar to the morphological evolution of large diamond crystals on the initially formed soot structure on Fe [6].

Even though the evolution of a dense structure can be explained by atomic unit deposition, the evolution of the porous structure shows in Figs. 1(a), 2(a)–(d) and Fig. 4(a) is difficult to explain. The porous structure can be best explained by landing of charged particles suspended in the gas phase like a colloidal suspension. A porous structure is commonly obtained by flocculation sedimentation in colloid chemistry, which occurs when van der Waals attraction between charged particles is dominant over Coulomb repulsion. If charged clusters approaching the surface lose charge quickly just prior to landing, only van der Waals attraction exists between the surface and clusters. In this case, the tendency for the random sticking of clusters on the surface can lead to a porous structure.

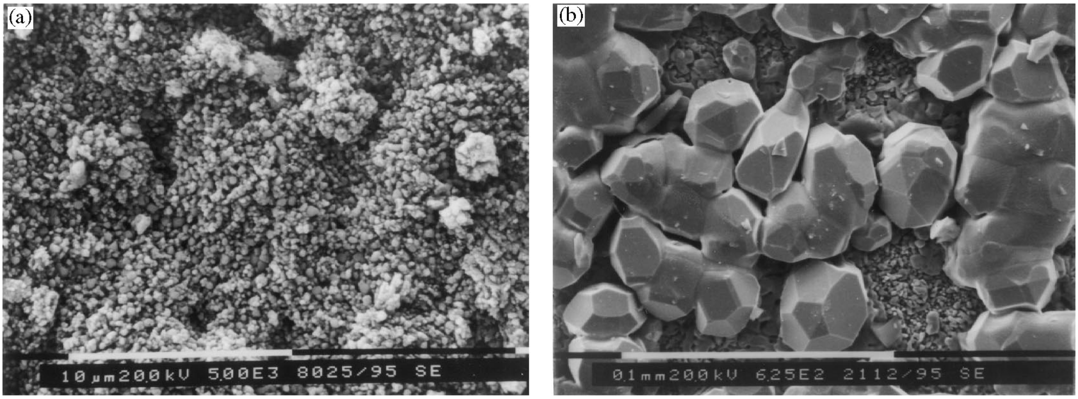

Fig. 4. SEM photographs of silicon deposits after (a) 3 and (b) 30 min on the Ni substrate with other conditions being the same as those for Fig. 1.

In this respect, charge appears to have crucial effects in making a dense film on a substrate of a low CTR in two respects. The one is the suppressing of Brownian coagulation between clusters in the gas phase, maintaining a nanosize. The second might be the selective landing on a macro kink-like corner, which might exert the least repulsive force to the incoming charged clusters. This property produces a three-dimensional self-assembly of clusters into a regular and compact array. This behavior resembles deflocculation sedimentation in colloid chemistry, which occurs when Coulomb repulsion between charged particles is dominant over van der Waals attraction. Besides, charged clusters appear to have higher atom mobility than neutral clusters. Otherwise, the dense microstructure evolution accompanied by a low growth rate in Fig. 1(b) would be difficult to explain.

The transition from an initially porous fine-grain structure (Fig. 4(a)) to large grains in the later stage (Fig. 4(b)) can also be explained by the two stages of deposition based on CCM. In the initial stage, the deposition behavior would be the same as that for any substrate with a high CTR and in a later stage after the Ni surface was covered with Si, the deposition behavior would be similar to any substrate with a low CTR.

The growth of large grains did not start immediately after the Ni surface had been covered with Si. It appears that the CTR changes gradually with Si deposition. The reason might be that some Ni atoms diffuse out over the growing surface during the process. As this diffusion flux decreases with increasing thickness of deposited Si, the CTR on the surface continues to decrease and eventually changed to the low CTR. In the case of a CVD diamond process, Huh [17] experimentally confirmed that the substrate materials such as Ni, Fe, Co and Pd were contained in the soot aggregates by transmission electron microscopy (TEM). He also showed that the soot particles grown on the Ni substrate, after being dispersed in methanol, were agglomerated by magnet. These results indicate that the substrate materials tend to diffuse out to the surface under the processing condition.

Since it is easiest for charged clusters to land on materials with a high CTR, some noble metals can be used to enhance selective deposition. In aluminum metal organic CVD, there is low selectivity between Al and SiO_2. However, it was reported that the selectivity between Al and SiO_2 can be enhanced by the sputter-deposition of thin Pd and Co layers on Al interconnection lines during selective deposition in Al CVD process [18]. We believe that the enhanced selectivity is related to the high CTR of Pd and Co, where charged Al clusters can land easily.

If charged clusters are suspended in the gas phase, the deposition behavior would be affected by electric bias applied to the substrate. We experimentally confirmed this effect [14]. In relation to this effect, a report by Lee et al. [19] regarding the Cu metallorganic CVD process is the only study where bias was applied to the system that the authors are aware of. They compared three cases of no bias, $-30\,\mathrm{V}$ and $+30\,\mathrm{V}$ on the substrate. For $+30\,\mathrm{V}$, the microstructure was not different from the case without bias. For $-30\,\mathrm{V}$, however, the nucleation and growth rate increased appreciably. Besides, a continuous copper layer covered the whole surface of the substrate at the bias of $-30\,\mathrm{V}$ while isolated islands were formed with a low island density of $\sim 3\,\mathrm{mm}^{-2}$ in the cases of no bias and $+30\,\mathrm{V}$. The sign dependence on the bias effect implies that clusters were mainly positively charged.

4. Conclusions

The dependence of the deposition behavior of silicon on various substrates was studied in the silicon CVD process. The dependence was explained by the CTR of substrates based on the CCM.

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