Low Temperature Amorphous Silicon Carbide Thin Film Formation Process on Aluminum Surface Using Monomethylsilane Gas and Trichlorosilane Gas

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The low-temperature chemical vapor deposition process of silicon carbide (SiC) on an aluminum surface was developed. In order to prepare the reactive substrate surface, a silicon interlayer containing silicon dimers at its surface was formed using trichlorosilane gas at 600 ºC. Next, the SiC thin film was formed at room temperature using monomethylsilane gas. Silicon, carbon and silicon-carbon bond in the obtained film were detected by various evaluations. The SiC film was amorphous and about 5-nm thick.

Keywords: silicon carbide, monomethylsilane, aluminum, room temperature

1. Introduction

Silicon carbide (SiC) is a suitable surface coating material, because its film is robust even in a harsh environment and at high temperatures. The typical application is the coating of the carbon susceptor used in a chemical vapor deposition (CVD) reactor [1]. However, because the temperatures for depositing the SiC film [2-4] is often higher than the melting point of various useful metals, such as aluminum, the SiC coating has been limited to only a few materials, such as carbon and silicon [4].

For achieving deposition on various metals, the low temperature amorphous SiC film formation technology using monomethylsilane (MMS) gas [5-10] is expected to be applicable and hopeful. This technology consists of two steps, that is, (A) the reactive surface preparation (formation of dangling bonds and silicon dimers), and (B) the SiC film formation from MMS gas at room temperature. In our previous studies, the reactive surface has been prepared using the three different processes, such as (I) the hydrogen annealing [5, 6], (II) the silicon interlayer formation [7, 10], and (III) the argon plasma etching [8]. Because Process (II) was shown to be possible on an aluminum surface [10], the characteristics of the SiC film and the silicon interlayer should be studied further.

In this study, the low-temperature process of amorphous SiC film deposition on an aluminum substrate was performed and evaluated using the silicon interlayer.

2. Experimental

The film formation process used in this study is shown in Fig. 1. The silicon thin film is formed at 600 °C on the aluminum surface using trichlorosilane (TCS) gas, as shown in Fig. 1 (b). The substrate is then cooled to room temperature in ambient hydrogen. Because the silicon interlayer surface has silicon dimers as shown in Figs. 1 (b) and (c), the amorphous SiC film can be produced using the MMS gas, as shown in Figs. 1 (c) and (d). The substrates used in this study were aluminum plates, the dimensions of which were 10-mm wide, 10-mm long and 0.1 – 0.3-mm-thick.

In order to obtain the silicon interlayer by the CVD method, the horizontal reactor [5-7, 10] shown in Fig. 2 was used. This reactor consisted of a gas supply system, a quartz chamber and infrared lamps. The gas supply system can introduce gases of hydrogen, nitrogen, TCS and MMS. Hydrogen gas is the carrier gas in the reactor used at 1×10^5 Pa and typically at the flow rate of 1 slm. The TCS and MMS gases diluted by hydrogen gas were used for the deposition of the silicon and SiC, respectively.

Fig. 3 shows the steps for producing the silicon interlayer and the SiC film. During Step (A), the silicon thin film was produced using TCS gas at 0.06 slm for 10 min at 600 °C. This film was cooled to room temperature in ambient hydrogen. In Step (B), the SiC film was formed at room temperature using MMS gas at 0.1 slm for 7 min.

In order to evaluate the very thin SiC film formed on the silicon surface, a Time-of-Flight Secondary Ion Mass Spectrometer (ToF-SIMS), a Transmission Electron Microscope (TEM) and, a energy dispersive X-ray spectrometer (EDX) were performed.

3. Results and Discussion

Fig. 4 shows the depth profiles of Al_2O_3, SiC_2, C_3, Si_4 and Si_2O_5 in the film obtained following the process shown in Fig. 3 on the aluminum substrate. The species deeper than 1 nm was attributed to aluminum oxide. Si_4 has a peak at the depth of 0.8 nm from the surface, because the silicon thin film was in the range of 0.4 – 1 nm depth. The SiC film corresponds to the peak of SiC_2 at the depth of 0.3 nm. Additionally, the C_3 peak at about 0.2 nm from the surface was found; this position was the same as that of the silicon oxide, Si_2O_5. Although the C_3 peak might be mainly assigned to SiC, the peaks of C_3 and Si_2O_5 could be the by-product of the MMS oxidation. A part of the chemisorbed MMS still remaining in the intermediate form, as shown in Fig, 1 (d), was oxidized to form silicon oxide and a carbon layer at the surface.

A TEM image of the obtained film was taken and shown in Fig. 5. The silicon interlayer was intentionally formed thick in order to clearly observe the stacked layers and their interface. Fig. 5 (a) shows the overall view of the obtained film. At the bottom of Fig. 5 (a), there was the aluminum substrate. The thin and low contrast layer on the aluminum substrate was aluminum oxide. The thick silicon interlayer existed on the aluminum oxide layer; the SiC film existed on the silicon interlayer. The TEM image additionally showed that that the interfaces between the aluminum oxide/silicon interlayer and silicon interlayer/SiC were abrupt without any void in this region.

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Fig. 5 (b) shows the high resolution image of the SiC and the silicon interlayer. In this figure, each spot indicates atoms. The upper half of this figure shows the non-periodic arrangement of the silicon and carbon atoms. This shows that the obtained SiC film was amorphous, similar to our previous study [8].

There were periodic spots in the lower left half of Fig. 5 (b), but non-periodic spots were observed in the lower right half of this figure. This shows the co-existence of silicon grains having various orientations formed on the aluminum oxide surface. Because this figure also shows that there was no void along the grain boundary in this region, the silicon thin film formation on the aluminum oxide surface is expected to be possible without a fatal defect.

The existence of silicon and carbon was evaluated using the EDX at four points in Fig. 5 (b). Points #1 and #2 are in the upper half and lower half region, respectively, of the amorphous SiC film. Point #3 is the silicon interlayer showing a non-periodic image; Point #4 is the silicon interlayer showing a periodic image.

Figs. 6 (a) and (b) show the existence of silicon and carbon at Points #1 and #2, respectively. This indicates that the film is SiC. A considerable amount of oxygen indicates the oxidation of the intermediate species remaining after the deposition. This result is consistent with the existence of Si_2O_5 in Fig. 4.

In the silicon interlayer, the major element was silicon, as shown in Figs. 6 (c) and (d). A small amount of carbon in these figures is considered to be carbon contamination that occurred during the operation of the TEM and EDX sample preparation. Because the profiles

of Figs. 6 (c) and (d) coincided with each other, the different appearance of the high resolution TEM image in the lower half of Fig 5 was due to the crystal grain orientation.

As shown in Figs. 6 (a) and (b), a small amount of aluminum was present in the amorphous SiC film. Because aluminum was not present in the silicon interlayer as shown in Figs. 6 (c) and (d), aluminum was not incorporated during the silicon interlayer formation process at 600 °C. Taking into account that aluminum chloride is a volatile material [11], and also that the aluminum amount was higher in the lower region of the amorphous SiC film, the aluminum chloride formed and vaporized at the aluminum substrate surface might be adsorbed at the silicon interlayer surface during the cooling process between Steps (A) and (B) in Fig. 3. Following such a process, aluminum might be incorporated in the amorphous SiC film. The aluminum incorporation is considered to correspond to the dark contrast region at the lower position of the amorphous SiC film in Fig. 5 (b).

For achieving a good coating film, the film and interface should be evaluated over a wide area. Figs. 7 and 8 shows the TEM image of the films and layers on aluminum substrate, produced using the same condition as that in Fig. 5. Figure 7 shows the films and interfaces between aluminum, aluminum oxide, silicon and silicon carbide. Each interface is shown to be abrupt and no void over 500 nm length. This indicates that the silicon nucleation uniformly occurred at the aluminum oxide surface, not in the gas phase, for producing uniform and dense film, even the aluminum oxide surface was not *in-situ* cleaned before the silicon interlayer formation. Figure 8 additionally shows the magnified image of the interface

between the silicon carbide and silicon. Over nearly 100 nm length, the interface is very clear and abrupt. This indicates the bonding between the layers of silicon carbide and silicon was built following the mechanism consistent with that shown in Fig. 1, not by the other processes, such as the gas phase nucleation.

The low temperature process employing the silicon interlayer as the reactive surface was successful in producing a SiC film on the aluminum surfaces. Because the highest temperature in this process was 600 $^{\circ}$C, the SiC coating process shown in Figs. 1 and 3 is expected to be possible as a low temperature process for SiC coating on aluminum.

4. Conclusions

The thin film formation process of amorphous SiC on an aluminum surface was developed. In order to produce a surface which was reactive to MMS gas, the silicon interlayer on the aluminum surface was formed by means of a thin silicon film deposition using TCS gas at 600 $^{\circ}$C. After cooling to room temperature in ambient hydrogen, the amorphous SiC thin film was formed at room temperature and at atmospheric pressure using MMS gas. The various evaluations showed that the film obtained on the polysilicon interlayer was amorphous and consisted of SiC. A low-temperature amorphous SiC film formation process on an aluminum surface is possible.

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Figure captions

Figure 1 SiC film deposition process using silicon interlayer (Process (II)).

Figure 2 Horizontal cold-wall CVD reactor used for film deposition of silicon and SiC.

Figure 3 Steps for formation of silicon (silicon interlayer) and amorphous SiC film. Step (A):

silicon film formation for 10 min at 600 $^{\circ}$C using TCS gas at 0.06 slm. Step (B):

Amorphous SiC film formation at room temperature using MMS gas at 0.1 slm for 7

min.

Figure 4 Depth profiles of Al_2O_3, SiC_2, C_3, Si_4 and Si_2O_5 in the film obtained on aluminum

substrates measured by ToF-SIMS. Amorphous SiC film deposition was performed

after the silicon interlayer formation at 600 $^{\circ}$C and cooling in ambient hydrogen.

Figure 5 TEM image of the film obtained on aluminum substrates using 6% TCS gas at 600

$^{\circ}$C and 10 % MMS gas at room temperature. (a): Overall view of the obtained film

consisting of an aluminum substrate, aluminum native oxide, silicon interlayer and

SiC film. (b): High resolution image of SiC film and silicon interlayer. EDX was

performed at the four points of #1-4.

Figure 6 Silicon, carbon, oxygen and aluminum in the SiC film and the silicon interlayer

measured by EDX. (a), (b), (c) and (d) are the normalized counts at #1, #2, #3 and #4,

respectively, in Fig. 5.

Figure 7 Wide TEM image of the films and interfaces on aluminum substrates.

Figure 8 TEM image of the interface between silicon carbide film and silicon film.