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Reduction of vacuum sublimation by ion beam treatment for e-beam deposited SiC films

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ABSTRACT

We report on the low temperature (≤1000 °C) vacuum sublimation behavior of e-beam evaporative deposited SiC film and a method to reduce the vacuum sublimation by an ion beam process. The density of SiC film deposited by e-beam evaporation method was ~60% of the density of bulk source material. In this sample, we found that sublimation became appreciable above ~750 °C under 1.5 × 10^{-5} torr pressure and the sublimation rate increased with increasing temperature, reaching ~70 nm/h at 950 °C when the coated sample was heated for 5 h. When the film was irradiated with 70 keV N^+ ions prior to heating, the sublimation rate decreased down to ~23 nm/h at a fluence of 1 × 10^{17} ions/cm^2. However, further increase in fluence beyond this value or extended heating period did not change (decrease or increase) the sublimation rate any more.

1. Introduction

It is known that a commercial bulk SiC can be grown by sublimation at a temperature range of 1600 °C–2500 °C under 1 × 10^{-3} torr–2 × 10^{-2} torr pressure [1–4]. In such a temperature regime, the film growth rate is as high as a few tens of μm/h. The growth rate is always smaller than the mass transport (sublimation) rate of a source SiC and usually it is limited by the mass transport rate [5]. In this work, we found that the sublimation occurred even below 1000 °C under low pressure (≤2 × 10^{-5} torr) conditions for films deposited by e-beam evaporation, although the sublimation rate was much low. The density of deposited films was low compared to that of the bulk source material. Such low density films tended to sublimate at low temperatures under high vacuum. The low density is largely due to the crystalline defects that are incorporated in the film during deposition, typical for the ceramic films deposited at low temperatures [6,7]. The vacuum sublimation of the deposited film not only reduced the film thickness but also deteriorated the film composition [8]. Therefore, should the deposited film be used under high vacuum and high temperature environment, the effect of sublimation must be taken into consideration, or a method to reduce such sublimation must be devised.

The original object of this work was to develop SiC coating to protect metallic components to be used above 900 °C in vacuum [9,10], but unexpectedly the coating sublimated even at lower temperatures. In this paper, therefore, we study systematically the low temperature sublimation behavior of the e-beam deposited SiC film by annealing the film below 1000 °C under high vacuum, and do our endeavor to develop a method to reduce sublimation by ion beam treatment.

2. Experimental

SiC films were deposited by electron beam evaporation on metallic substrate (Alloy HX sheet: ~15 × 15 × 0.5 in mm), after polishing off the surface layer of the substrate to 0.5 μm with diamond paste. The system used in this work is equipped with an e-beam evaporator and a 150 keV ion accelerator in the same chamber so that the coating and ion beam process could be conducted in-situ without breaking the vacuum. Prior to SiC deposition, the sample surface was sputter-cleaned further for 10 min with 10 keV N^+-ions at a beam current of 0.5 A. The base chamber pressure was ~1 × 10^{-5} torr and the operational pressure during e-beam deposition was ~5 × 10^{-5} torr. The SiC film was then deposited to a thickness of ~50 nm by e-beam evaporation, followed by ion beam mixing with N^+-ions at 70 keV to a fluence of ~5 × 10^{16} ions/cm^2. In our previous work, it was found that this preparatory ion beam mixing was necessary to ensure adhesion and prevent inadvertent peeling by thermal stresses during heating and cooling cycles [10]. Additional SiC was deposited to make the total film thickness ~1 μm at a deposition rate of 3 Å/s with 0.15 A electron beam current. The substrate temperature during the e-beam deposition was 150 °C. Subsequently, the deposited film was bombarded by 70 keV N^+-ions to a fluence of ~1 × 10^{17} ions/cm^2

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Table 1
Relative atomic concentrations of the film measured by XPS spectrum as a function of depth from the surface.

Surface condition	O 1*s* (%)	C 1*s* (%)	Si 2*p* (%)
On the as-deposited film surface	31.16	35.63	33.21
After 15 nm sputtering	17.48	35.24	47.28
After 30 nm sputtering	15.04	37.01	47.95
After 45 nm sputtering	14.68	37.18	48.14
After 60 nm sputtering	13.35	39.68	46.96

to $\sim 4 \times 10^{17}$ ions/cm^2. The film thickness and deposition rate were determined by using a gold plated quartz crystal, with additional confirmation by SEM cross sectional examination. The samples were then placed in an alumina boat and heated in a quartz tube vacuum furnace at temperature ranges of 550 °C–950 °C for 5–10 h at $\sim 1.5 \times 10^{-5}$ torr. The metal specimens were weighed before and after SiC deposition to determine the density of as-deposited SiC and the sublimation rate of annealed SiC using a micro balance with a readability of 0.01 mg (a repeatability of 0.02 mg).

A VG science model ESCALAB 210 was used for the XPS analysis of the coating layer before and after annealing. The peak scans were obtained for each sample using 1253 eV Mg Kα X-rays and an analyzer pass energy 50 eV over the binding energy range from 1 to 550 eV.

SRIM software [11] was employed to estimate the peak ion stopping range during ion bombardment onto the deposited film.

3. Results and discussion

The atomic concentrations of O, C, and Si in the as-deposited film were measured by XPS, and are listed in Table 1. The XPS analysis shows that the surface oxygen concentration is high, ~31 at.%, which is reduced to 13.35 at.% after the surface layers are sputtered away to 60 nm depth, making the remaining composition close to the stoichiometric SiC. This peculiar compositional gradient across the deposited film is thought to be due to a post-deposition oxidation of the e-beam deposited SiC film in view of high activity of freshly deposited film and diffusion limited process of oxidation during exposure to air, prior to XPS analysis. The diffusion scenario is further justified in view of the high porosity of the deposited film as described below. Although a certain amount of silicon oxides exists together with Si and C in the deposited film, we assume the film is mostly SiC in the analysis.

From the measurements of weight changes, SiC film thickness, and the surface area of the sample, the density of the SiC film was found to be about 1.92 g/cm^3. This value is about 40% lower than that of the bulk SiC (3.217 g/cm^3) [12]. As mentioned already, the ceramic coatings do not adhere well on the metallic surface and thus are prone to peel off during thermal cycles, negating the benefits of high temperature thermal and chemical resistance of ceramics. Therefore, additional treatments are necessary to warrant its usefulness. In our previous work, the adhesion was proven to be improved by ion-beam mixing (or stitching) of the ceramic/metal interface [13–17]. In this work again, we used N^+-ion beam to produce a highly adherent coating layer by mixing the atoms at the metal–SiC interfacial region.

We used N^+-ions deliberately instead of inert gas ions to mix the interface region and at the same time to reinforce the base materials by nitriding with the implanted nitrogen atoms. Our SRIM calculation suggests that the ion range in the 50 nm thick SiC fim/Alloy HX substrate generated by 70 keV N^+-ion bombardment is approx. 150 nm depth from the surface, suggesting both the interfacial mixing and the ion-implanting into the substrate should have occurred. We believe this may have somehow contributed to the enhanced adhesion because the nitrided part of the base metal near the interface may have played a role of a functionally graded layer, increasing a load bearing capacity. As expected, the ion beam mixing improved the adhesion: The ion beam mixed SiC film was still intact on the metal substrate after heating to 950 °C for 5 h although the difference in the thermal expansion coefficients is more than 3 times (CTE of Alloy HX: 16.6×10^{-6} at 980 °C and CTE of SiC: 5.0×10^{-6} at 1000 °C), confirming the enhanced adhesion by ion beam mixing [18]. All annealing in this experiment was done for 5 h as mentioned already. Despite the improved adhesion, there was noticeable sublimation for the e-beam deposited SiC and the color of the film was changed from yellowish to grayish after annealing to 950 °C. The color change may be associated with both

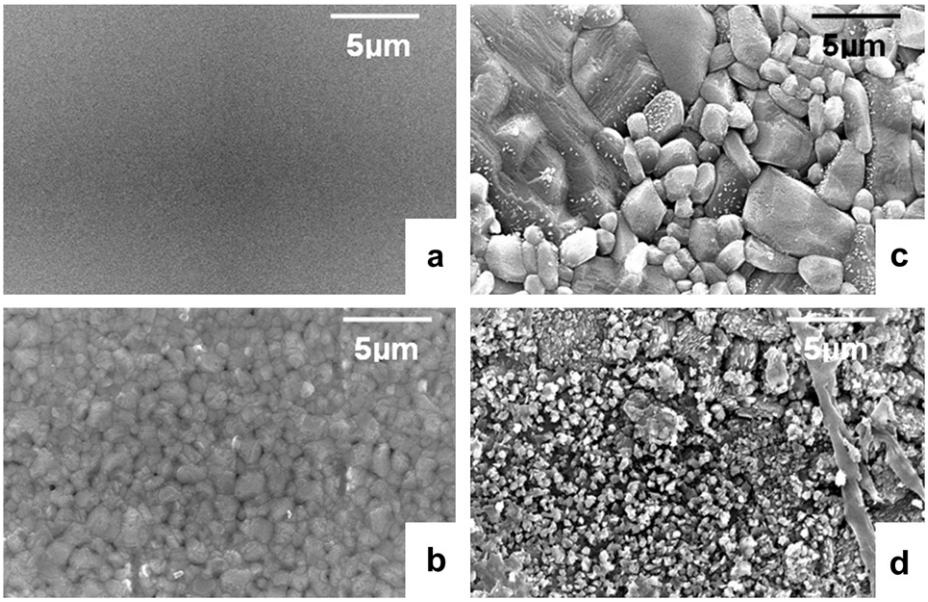

Fig. 1. Surface morphologies of as-deposited SiC film (a), SiC film annealed at 950 °C under $\sim 1.5 \times 10^{-5}$ torr pressure (b), as-received alumina (c), and deposition of sublimated SiC on the alumina surface (d).