Residual Stress and Elastic Modulus of $Y_2O_3$ Coating Deposited by EB-PVD and its Effects on Surface Crack Formation

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ABSTRACT

Recently, a new $Y_2O_3$ coating deposited using the EB-PVD method has been developed for erosion resistant applications in fluorocarbon plasma environments. In this study, surface crack formation in the $Y_2O_3$ coating has been analyzed in terms of residual stress and elastic modulus. The coating, deposited on silicon substrate at temperatures higher than 600°C, showed itself to be sound, without surface cracks. When the residual stress of the coating was measured using the Stoney formula, it was found to be considerably lower than the value calculated using the elastic modulus and thermal expansion coefficient of bulk $Y_2O_3$. In addition, amorphous $SiO_2$ and crystalline $Al_2O_3$ coatings were similarly prepared and their residual stresses were compared to the calculated values. From nano-indentation measurement, the elastic modulus of the $Y_2O_3$ coating in the direction parallel to the coating surface was found to be lower than that in the normal direction. The lower modulus in the parallel direction was confirmed independently using the load-deflection curves of a micro-cantilever made of $Y_2O_3$ coating and from the average residual stress-temperature curve of the coated sample. The elastic modulus in these experiments was around 33 ~ 35 GPa, which is much lower than that of a sintered bulk sample. Thus, this low elastic modulus, which may come from the columnar feather-like structure of the coating, contributed to decreasing the average residual tensile stress. Finally, in terms of toughness and thermal cycling stability, the implications of the lowered elastic modulus are discussed.

Key words : Yttrium oxide, Residual stress, Elastic modulus, Nano indentation

1. Introduction

The semiconductor industry uses many ceramics as plasma-facing materials. The plasma usually consists of reactive radicals and ions from fluorocarbon gases, which react with the ceramics, causing erosion. Aluminum oxide is a typical plasma resistant material and yttrium oxide is increasingly used because of its higher plasma resistance. Even though yttrium oxide is very effective as a plasma resistant material, it is too expensive to be applicable in sintered parts because of the considerable consumption cost of this rare-earth oxide. To solve this difficulty, plasma-sprayed coatings have been widely used in the semiconductor industry during the last decade. Recently, however, this kind of coating process is being studied as a potential source of harmful particulate contamination as semiconductor devices are scaled down to 20 nm. Generally, plasma sprayed coatings consist of lamellar structures and thus their bonding strength to the substrate is around a few MPa. In addition, very rough coating surfaces and surface cracks may aggravate preferential erosion, possibly resulting in the formation of many particles.

In order to overcome the shortcomings of the plasma-sprayed $Y_2O_3$ coating process, new techniques have been developed to produce nano-structured $Y_2O_3$ coatings; these coatings have multiple times higher bonding strength than those of plasma-sprayed coatings. Aerosol deposition and electron-beam evaporation methods are typical examples of the new coating methods. Aerosol deposition can be done at room temperature and yields nano grains with high plasma resistance. On the other hand, electron beam PVD (EB-PVD) provides large area deposition at fast coating speeds and allows for a smooth surface application. However, the structural reliability of these coatings has rarely been investigated. As a plasma-facing material, the coating’s chemistry may determine the average etch rates, but the material’s practical applicability depends on the reliability of the coating, which is strongly influenced by defects such as cracks formed during subsequent cooling after deposition.

Because a coating is bonded to a substrate, a residual stress may develop due to thermal expansion mismatch between the substrate and the coating, producing cracks on the coating surface. The residual stress $\sigma$ due to thermal expansion mismatch has been calculated for the temperature difference $\Delta T$ between deposition and room tempera-

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ture using the following equation:\(^{(11)}\)

\[
\sigma_r = \frac{E_c}{1-v_c} (\alpha_c-\alpha_s) \Delta T
\]

(1)

where \(\alpha_c\) and \(\alpha_s\) are the average thermal expansion coefficients of the substrate and coating in the temperature range \(\Delta T\), and \(E_c\) and \(v_c\) are the Young’s modulus and Poisson ratio of the coating, respectively. Generally, in order to avoid premature delamination of a coating from its substrate, the substrate temperature should be sufficiently increased to enhance adhesion; that process, however, will raise \(\Delta T\), and, hence, residual stress due to thermal expansion mismatch increases at the same time. So, the substrate temperature is a critical processing parameter that must be optimized. However, it is not easy to predict the residual stress using Eq. 1, because coatings usually do not have isotropic microstructures, and thus the calculation may contain many uncertainties concerning Eq. 1’s parameters.

In the present study, we first observed the cracking behavior of \(\text{Y}_2\text{O}_3\) coating as a function of the deposition temperature. Then, the residual stress of the coating was estimated quantitatively by measuring the surface curvature of the coating. For comparison, amorphous \(\text{SiO}_2\) and crystalline \(\text{Al}_2\text{O}_3\) coatings were prepared and their residual stresses were measured. The measured stress was analyzed in terms of the microstructure of the coating. In order to determine the mechanical properties of the \(\text{Y}_2\text{O}_3\) coating with respect to the measurement direction, nano-indentation was applied to both the surface and the cross-sectional area of the coating. To confirm the elastic constant of the \(\text{Y}_2\text{O}_3\) coating, two independent methods, including measuring the micro-beam deflection and measuring the residual stress variation with substrate temperature, were applied. Based on the experimental results, the potential benefits of \(\text{Y}_2\text{O}_3\) coating from EB-PVD for a new plasma resistant material have been discussed.

2. Experimental Procedure

Using the EB-PVD method, \(\text{Y}_2\text{O}_3\) coatings were deposited on (100) planes of silicon wafer at temperatures of 150, 300, and 600°C. For comparison, \(\text{Al}_2\text{O}_3\) and \(\text{SiO}_2\) were similarly coated on the same substrate at 600°C. Commercially available \(\text{Y}_2\text{O}_3\) (1 ~ 2.5 mm, 99.99%, Taewon Scientific Co., Korea), \(\text{SiO}_2\) (1 ~ 3 mm, 99.99%, Taewon Scientific Co., Korea) and \(\text{Al}_2\text{O}_3\) (1 ~ 2.5 mm, 99.99%, Taewon Scientific Co., Korea) granules were used as source materials for the electron beam evaporation method. The base pressure before coating was around 5 \times 10^{-6} \text{ Torr} and the deposition rate was set at around 10 Å/sec by controlling the electron beam power. The coating thickness was varied between 0.5 and 4 μm. The average residual stress of the coating, \(\sigma_r\), was measured using the Stoney formula\(^{(10)}\)

\[
\sigma_r = \frac{E_c d_t^2}{6R(1-v_c)d_i}
\]

(2)

where \(R\), \(E_c\), \(v_c\), \(d_t\) and \(d_i\) are the radius of curvature of the coated sample, the Young’s modulus, the Poisson ratio, the thickness of the substrate, and the thickness of coating, respectively. The radius of curvature of the coating was measured using a surface profiler (Surfcorder ET3000, Kosaka Lab., Japan). Surface microstructures were analyzed using optical microscopy and scanning probe microscopy (SPM, JSPM5200, Jeol Co. Ltd, Japan). The cross-sectional microstructures were observed using transmission electron microscopy (TEM, Tecnai F30 FEI Co, Netherlands). In order to obtain the elastic modulus and hardness, nano-indentation (Triboindenter, Hysitron Co., USA) was applied. Surfaces and cross-sections of the coating were polished using a 1 μm diamond paste; then, the surface was carefully rinsed using high purity ethyl alcohol. The nano-indentations were conducted at a load of 10 mN using a Berkovich tip. For comparison, we prepared a micro cantilever of \(\text{Y}_2\text{O}_3\) coating. The cantilever patterns were made on the coating using a focused ion beam (FIB) operated with Ga⁺ ions at 30 keV and current of 9.3 nA; the silicon substrate was etched out with ethylenediamine pyrocatechol (EDP) solution for 120 min. Then, various vertical displacements were applied to the end point of the cantilever using nano-indentation in the displacement-control mode. From the load-displacement curve, we were able to calculate the elastic modulus in the direction parallel to the coating surface. Independently, it was possible to obtain the modulus from the variation of the surface curvature of the coating with respect to the increased temperatures; these curvatures were in-situ measured using a high curvatures stress measurement system (FSM500TC, FSM Co., Japan) from room temperature to 200°C.

3. Results

Figure 1 provides optical and SPM surface images of the coatings, which have thicknesses of 4 μm with increasing substrate temperature. Surface cracks can be seen to have developed in the coatings deposited at 150 and 300°C, but the coating deposited at 600°C showed no such cracks on the surface. Average crack spacing was wider for the coating deposited at 300°C than for the coating deposited at 150°C, indicating that coatings became more sound with increasing deposition temperature. The substrate temperatures also appeared to have an effect on the grain sizes, as can be observed in the SPM images. The grain size increased from 50 to around 200 nm with increase of the substrate temperature from 150 to 600°C. In terms of the homologous temperature \(T/T_m\), the ratio of the substrate temperature to the melting temperature of the coated material had values of 0.16, 0.21, and 0.32, respectively. So, at the two lower deposition temperatures, the coatings may have zone 1 structures, while the coating deposited at 600°C may have a zone 2 structure according to the structure zone model\(^{(13,14)}\). The fact that deposition at higher substrate temperatures produced fewer surface cracks might be contrary to the idea
that the tensile stresses of the coatings, due to thermal expansion mismatch, increase with increased temperature difference $\Delta T$ between the deposition temperature and the room temperature. If we take $3.5 \times 10^{-6}/K$ and $7.5 \times 10^{-6}/K$ for $\alpha_s$ and $\alpha_c$, and use $E_c$ and $v_c$ from bulk $Y_2O_3$ (160 GPa and 0.2 in eq. 1)), then the residual thermal stress for the coating deposited at 600°C deposition temperature can be calculated and found to be around 460 MPa in a tensile state; this value is significantly higher than the usual fracture strength of sintered $Y_2O_3$, which is usually around 180 MPa. However, no cracks were observed in the coating. Instead, decreasing deposition temperature, which would produce less thermal stress due to expansion mismatch, resulted in surface cracks. Furthermore, the crack spacing became narrower with decreasing deposition temperature. This behavior of the surface cracking might require more explanation rather than the simple calculation of thermal stress based on temperature difference provided above.

Actual average residual stresses of the coatings without surface cracks, which were deposited at 600°C, were measured using the Stoney formula for various coating thicknesses. The measured residual stresses of the coatings were between 60 and 110 MPa, much lower than the previously calculated value of 460 MPa (Fig. 2). For the tensile residual stress of the coating, the critical thickness, $d_c$, required to produce surface cracks can be calculated according to Eq. 3,$^{16,17}$

$$d_c = \frac{2}{\pi C_e} \left( \frac{K_{IC}}{\sigma_r} \right)^2$$

(3)

where $K_{IC}$ and $\sigma_r$ are the critical stress intensity factor and the residual tensile stress, respectively. $C_e$ is a numerical coefficient, 1.1213, describing a simple edge correction for a single-ended crack in a semi-infinite specimen. If we take 0.7 MPa m$^{1/2}$ for $K_{IC}$,$^{16}$ and 100 MPa for the residual stress, then the critical thickness is around 25 $\mu$m, which is thicker than the experimentally produced coating, confirming no surface crack formation. On the other hand, if the residual stress were 460 MPa, as in the simple calculation, the critical thickness would be around 1 $\mu$m, possibly resulting in surface cracks. In this way, despite the uncertainties of the fracture toughness and the limitation of the calculation model,$^{16,18}$ the reduction in the tensile stress appears to play a key role in producing a sound coating without surface cracks.

To understand the low residual stress of the coating deposited at 600°C, we observed the coating microstructures (Fig. 3). The microstructure consisted of fine columnar grains with a feather-like structure. The columnar feather-like structure has been one of the typical characteristics of thermal barrier coatings prepared using the electron-beam
evaporation method. The \( \text{Y}_2\text{O}_3 \) started to grow as very fine crystals on the silicon substrate and then in a columnar fashion during subsequent growth. In addition, we found an amorphous SiO\(_2\) layer as thin as 10 nm in the interface between the coating and the substrate. From these observed microstructures, two possibilities for the low residual tensile stress can be addressed. First, the tensile thermal stress of the coating during cooling is transferred to the amorphous layer, which may relax viscoelastically during cooling, resulting in the low thermal stress of the coating. Another possibility is that the feather-like columnar structure of the coating may have low elastic modulus in the direction parallel to the substrate. Since anisotropy of the Young's modulus in the thermal barrier coating prepared by EB-PVD has been reported in the literature, it can be considered in the \( \text{Y}_2\text{O}_3 \) coating, which has anisotropic columnar microstructures as shown in Fig. 3.

In order to check the possibilities, amorphous silicon dioxide and crystalline aluminum oxide were deposited at the same, \( T_s \), 600°C, and then average residual stresses at room temperature were compared to the values calculated based on Eq. 1. Fig. 4 shows the measured and calculated values for various thicknesses of amorphous SiO\(_2\) coating and, for comparison, of the Al\(_2\)O\(_3\) coatings. The residual stresses of the SiO\(_2\) coating were approximately the same as the calculated value, 150 MPa, regardless of the coating thickness, indicating virtually no viscoelastic relaxation of the amorphous layer. This appears to be a natural consequence of the fast cooling after the deposition and the very high viscosity of the amorphous SiO\(_2\) in the temperature range. Meanwhile, the deposited crystalline Al\(_2\)O\(_3\) showed much lower residual stresses than those calculated using the values of \( \alpha \) and \( E_c \) of the dense sintered bulk. Similar to the \( \text{Y}_2\text{O}_3 \) coating, the Al\(_2\)O\(_3\) coating showed columnar microstructures with no surface cracks. For comparison, the homologous temperature of Al\(_2\)O\(_3\) deposition was 0.37, slightly higher than that of the \( \text{Y}_2\text{O}_3 \) deposited at 600°C. Therefore, the lower residual stress of the \( \text{Y}_2\text{O}_3 \) coating may not be a result of the viscoelastic relaxation of the amorphous SiO\(_2\) layer between the coating and the substrate.

In order to observe the effects of the columnar structures on the elastic modulus, nano-indentations were applied on the top surface or cross-section of the \( \text{Y}_2\text{O}_3 \) coating (Fig. 5). There was a significant difference in the elastic modulus depending on the measurement direction, i.e., an elastic modulus of 80 GPa was measured in the direction normal to the coating surface; the value was 50 GPa in the parallel direction. On the other hand, coating hardness was relatively insensitive to the direction. This may be because plastic deformation is a volumetric process while elastic response is more dependent on the microstructure anisotropy. About the absolute values of the elastic modulus, as determined in the indentation experiment, however, we must be cautious because densification due to the high compressive stress during indentation loading may affect the unloading process and hence increase the elastic modulus. The coatings deposited by evaporation method usually have nanopores between the columnar grains which can be made denser by indentation. In addition, the coating surface is in a biaxial stressed state, while the cross-section is in a uniaxial state. However, though the absolute values of the elastic modulus may need some correction, the lower modulus in the direction parallel to the coating surface must have a significant effect on the residual stress of the coating because that modulus is used in Eq. 1.

Fig. 3. TEM microstructure of \( \text{Y}_2\text{O}_3 \) coatings deposited at 600°C.

Fig. 4. Measured and calculated residual stresses of Al\(_2\)O\(_3\) and SiO\(_2\) coatings deposited at 600°C with various thicknesses.

Fig. 5. Load-displacement curves for surface and cross-section of \( \text{Y}_2\text{O}_3 \) coating deposited at 600°C.
To overcome the uncertainties in the nano-indentation technique mentioned above, the elastic modulus in the direction parallel to the coating surface was measured from load-deflection curves of the micro-cantilever made of Y$_2$O$_3$.

Fig. 6 shows a cantilever with a width of 15 μm and a length of 50 μm; its typical load-deflection curve appears in Fig. 7.

For the deflection range of 0.4 ~ 1.0 μm, the elastic modulus in the direction parallel to the coating surface was determined to be 33 ± 3 GPa, which is somewhat lower than the previous value, 50 GPa, determined using nano-indentation.

The elastic modulus was also independently determined from the variation of the residual stress as a function of the measurement temperature for the same coating (Fig. 8). The slope of the residual stresses with respect to the temperature is usually considered as a function of the elastic modulus of the coating and the difference in the thermal expansion coefficients between the coating and the substrate, as in the following equation:

$$\frac{d\sigma_r}{dT} = \frac{E_c \Delta \alpha}{1 - \nu_c}$$

If we use $4 \times 10^{-6}$/K for $\Delta \alpha$, and 0.2 for $\nu_c$, a value of 35 GPa is obtained for $E_c$; this measurement is in the direction parallel to the coating surface. So, these independently determined elastic moduli showed similar values, in a range of 33 ~ 35 GPa.

From this experimental evidence, the presence of a surface without crack formation must be attributed to the lowered residual stress due to the lowered elastic modulus in the direction parallel to the coating surface. Then, the residual stress due to thermal expansion mismatch can be calculated using $E_c \approx 35$ GPa, $\Delta \alpha \approx 4 \times 10^{-6}$/K, $\nu_c \approx 0.2$, and $\Delta T \approx 570^\circ$C, resulting in $\sigma_r \approx 100$ MPa, which is quite close to the values observed in Fig. 2. Further, the critical thickness for crack formation, determined using Eq. 3, is as high as 25 μm, producing a sound coating without surface cracks, as shown in Fig. 1(c).

Actual situations, however, might be slightly complicated. As can be seen in Fig. 6, the free-standing cantilever is slightly curved, implying that there is a stress distribution along the thickness. That kind of stress-distribution has been studied for several systems but its mechanism has not been completely determined yet. In our specific case, it seems to be related to the thin amorphous SiO$_2$ layer under the Y$_2$O$_3$ cantilever, which is not removed by EDP solution.
4. Discussion

Although the low residual stress of the coating may be understood based on the reduction of the elastic modulus in the parallel direction, crack spacing with respect to deposition temperature needs more discussion. If the periodic array of cracks is assumed to be simultaneously driven by residual stress, the crack spacing, \( \lambda \), is determined by the balance per unit crack advance between mechanical energy release, \( W_m \), and separation energy of the homogeneous coating, \( W_c \):

\[
W_m = f \left( \frac{\lambda}{d_o} \right) \sigma_c \frac{d^2}{E_c},
\]

\[
W_c = 2\gamma_c \cdot d_o.
\]

Here, \( f(d_o) \) is a function describing the reduction of mechanical energy release with decreasing crack spacing \( \lambda \); \( \gamma_c \) is the surface energy of the coating. By equating \( W_m \) and \( W_c \) the possible crack spacing, \( \lambda \), can be determined. For the same \( \sigma_c \), the crack spacing decreases with decreasing \( \gamma_c \). For the same \( \gamma_c \), the spacing increases with decreasing \( \sigma_c \). In this way, the narrow crack spacing from the coating deposited at 150°C means that the \( \gamma_c \) of this coating might be much lower than those from the higher deposition temperatures. In the fracture of brittle solids, toughness, \( T_o \), is related to the surface energy and elastic modulus according to the following equation:

\[
T_o = (2E_c\gamma_c)^{1/2}.
\]

So, narrower crack spacing at lower deposition temperature means a qualitatively lower fracture toughness of the coating. Therefore, the deposition temperature in the evaporation method may affect the mechanical properties in various ways, including the hardness, elastic modulus, and fracture toughness, which must be related to the microstructural development of the coating.

Plasma resistant \( \text{Y}_2\text{O}_3 \) coatings in the semiconductor industry require high mechanical reliability; they must prohibit surface cracks and spalling inside the wafer processing chamber. This is especially true when the coating is exposed to thermal cycling due to the intermittent introduction of plasma because the plasma is a strong heat source. Usually, the temperature variation inside the processing chamber induces inhomogeneous stress distribution on the wall materials, resulting in surface defects. These surface defects are vulnerable to attack by radicals and ions with kinetic energy, which aggravate the defects and induce total failure of the coating. So, the formation of surface defects, typically cracks, must be suppressed even during abrupt temperature changes. Then, the high mechanical compliance that stems from low elastic modulus may be an important factor for reducing excessive stress generation and improving the reliability of the coating. In these respects, the columnar \( \text{Y}_2\text{O}_3 \) coating deposited using the EB-PVD method will be a strong candidate for a new plasma-facing material.

5. Conclusions

The surface cracking behavior of \( \text{Y}_2\text{O}_3 \) coatings with respect to deposition temperature has been investigated based on residual stress measurement and microstructural development. It was found that the measured residual stress of a coating deposited at 600°C was much lower than the value calculated based on the elastic modulus of bulk \( \text{Y}_2\text{O}_3 \). Nano-indentation on the \( \text{Y}_2\text{O}_3 \) coating showed that the elastic modulus varied depending on the measurement direction, with a lower value in the direction parallel to the coating surface. This lower elastic modulus in the parallel direction was confirmed by two independent methods: one that used the load-deflection response of a \( \text{Y}_2\text{O}_3 \) micro-cantilever and another that looked at variations in the surface curvature of the coated sample with increasing measurement temperature. The elastic modulus determined in these experiments was in the range of 33 - 35 GPa, which is much lower than that of the sintered bulk. The lower elastic modulus in the parallel direction may be a result of the columnar feather-like structures of the coating, which is one of the characteristics of coatings deposited using the evaporation method. Therefore, the reduced elastic modulus contributed to the lower tensile residual stress of the coating, resulting in no surface cracks when the coating was deposited at 600°C. The developed \( \text{Y}_2\text{O}_3 \) coating may provide high mechanical stability due to its high compliance; it should also provide a high plasma resistance, making it suitable for applications in corrosive plasma environments.

REFERENCES