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Auger Analysis Across an Interface Between Cr Film and Pure Silica[†]

Yasuo TAKAHASHI*, Katsunori INOUE**, Kunio TAKAHASHI*** and Kimiyuki NISHIGUCHI****

Abstract

The valence Auger spectra across the interface between Cr film and pure SiO₂ glass (Cr/SiO₂) are measured after annealing and compared with that of Cr film on a Si wafer (Cr/Si) for the purpose of understanding the chemical bonding across the interface between metals (films) and ceramics (substrates). It is observed in the interface of Cr/SiO₂ after annealing that oxygen and chromium more preferentially diffuse than Si. It is found from the Auger-intensity-ratio that a Cr-Si bond is formed at the interface as a result of the diffusion of Cr into SiO₂-substrate, although no silicide layers are observed. This Cr-Si bond is much more metallic than an Si-O bond according to the difference in the kinetic energy of Auger electrons. On the other hand, oxygen takes electrons from the 3d state of Cr atom by diffusing into the Cr film. A Cr-O bond is consequently formed in the metal side of the interface. It is suggested that the monotonical change in electronic structure is achieved across the interface of Cr/SiO₂. Both Cr-O bonds and Cr-Si bonds are formed as a result of the monotonical change in the electronic structure.

KEY WORDS: (Auger Spectroscopy) (Valence Electronic Structure) (Chemical Bonding) (Thin Film) (Chromium) (Fused Quartz) (Interface)

1. Introduction

Recently, hybrid materials have been applied to many fields of manufacturing. In particular, metals and ceramics are one of the most important couples for hybridization, for example metal films on ceramic substrates. It has been said that the segregation of IIIa-VIa elements at the interface between metals and ceramics plays an important role for tight joining¹⁻⁴). It has also been accepted that the oxidation of a metal surface before bonding contributes to attaining high bond strength⁵⁻⁷). These facts suggest that the distribution of these elements across the interface is significant for strong adhesion. Comprehending the chemical bonding at the interface is essential to understanding these facts. It is then necessary to observe the valence electronic structure. There must be a transition of the valence electronic structure across the interface because the valence level of ceramics is much deeper than that of metals⁸⁻¹⁰). There are, however, few studies to observe the actual transition of the electronic structure, from the view point of the local chemical bonding, between elements even for the simplest system such as Cr/SiO₂.

In the present study, Auger electron spectroscopy is

used to discuss the chemical bonding across the interface. Pure SiO₂ is employed as a ceramic substrate containing oxygen because the valence electronic structure of SiO₂ is widely known^{11,12}). The influence of impurities is neglected. Chromium is adopted as a metal film among the IIIa-VIa elements. Chromium has five electrons in its 3d state, which plays an important role in the chemical bonding at the interface. The number five is large enough to observe the change in Auger signal associated with 3d electrons. The interface of a Cr film on a Si wafer is also investigated in order to understand the role of oxygen. The Auger analysis of this interface (Cr/Si) gives a suggestion of the Cr-Si bond. This is a useful hint if Cr-Si bonds are formed at the interface of Cr/SiO₂^{5,13}).

Table 1 Spectroscopic symbols and corresponding orbitals.

Symbol	K	L ₁	L ₂₃	M ₁	M ₂₃	M ₄₅
Orbital	1s	2s	2p	3s	3p	3d

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2. Prior work

Figure 1 schematically illustrates Si-DOS in SiO_2 . The V_1 and V_2 are the energies of the valence orbitals and the defect level D^{14} . According to refs.14-17), the energy distribution of the $L_{23}V_1V_2$, Auger electrons $N(E_A)$ is obtained by

$$N(E_A) = \int W_A(V_1, V_2, \epsilon) \cdot n(V_2 - \epsilon) \cdot n(V_1 + \epsilon) d\epsilon \quad (1)$$

where W_A is the matrix element for the Auger transition, and n is the electronic local DOS. W_A is generally assumed to be constant in taking into account the Auger transition¹⁴⁾, although the band width is sometimes too narrow to regard W_A as a constant^{18,19)*}.

Then, the Auger intensity is proportional to the product of the two local DOS about both systems of Cr/ SiO_2 and Cr/Si. It is possible to observe the transition of the occupied local DOS through the interface by measuring the change in the Auger intensity. The Auger intensity, however, depends on the concentration of the elements. We must calibrate the intensity by the component due to the concentration. We take the ratio of two appropriate intensities derived from a same spectrum. For example, the intensity ratio of Cr- $L_3M_{23}M_{45}$ /Cr- $L_3M_{23}M_{23}$ corresponds to the ratio of M_{45} -state/ M_{23} -state in number of electrons. We can discuss the change in M_{45} electrons per one Cr-atom.

3. Experiment

Chromium was deposited onto the pure SiO_2 glass substrate (impurities < 0.5ppm) and onto the Si wafer by electron beam deposition resulting in a thin film with a thickness of 100nm. After the deposition, the specimens were annealed at 1073K for 1800s (or at 723K for 3600s). This annealing made it easy to analyze the local Auger transition process because the treatment broadens the interface.

The JAMP10S instrument made by JEOL was used for measurements. Specimens were etched by Ar^+ ion (acceleration voltage: 2kV, emission current: 30mA, absorbed current: 1.5×10^{-7} A, spot-mode). The Auger spectra were measured across the interface between the film and the substrate under the vacuum condition of 1×10^{-7} Pa. The primary electron beam (5keV, 35mA) was focused to a spot of about 50nm diameter. The incident angle was to 75 deg., resulting in the absorbed current of less than 1.5×10^{-8} A. The primary electron

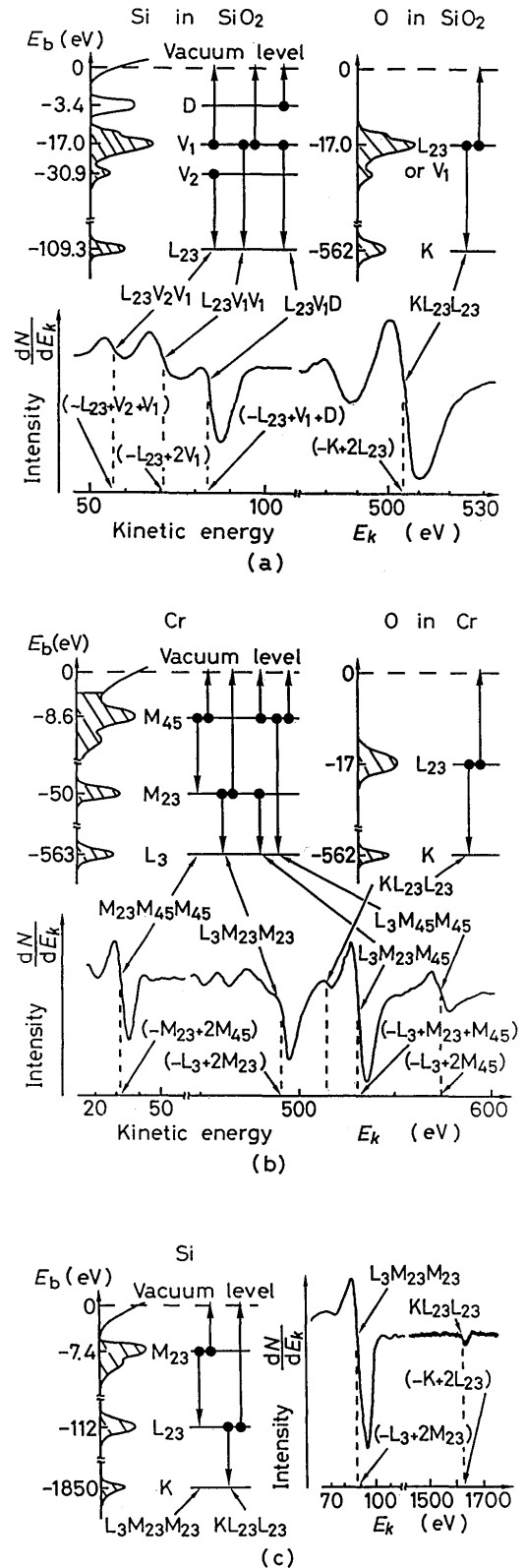


Fig. 1 Schematic illustrations of Si-DOS in SiO_2 . The V_1 is the upper valence band, V_2 the lower valence band¹²⁾ and D is the surface defect level¹⁴⁾.

*The authors consider that the band widths in our systems (Cr/ SiO_2 , Cr/Si) are not so narrow. We need not take the change in W_A into consideration. We regard W_A as a constant in this study.

dose was kept constant for each specimen (irradiation period = 640s). It was difficult to analyze integrals of spectra (BBM mode) because of the background of the spectra. We adopted the derivative data in order to estimate the intensity more accurately. The intensities of Auger electrons were mainly defined as the peak-to-peak values around the inflection points of Auger differential spectra. The value from the lower peak to the inflection point was adopted when the upper peak of the Cr-L₃M₂₃M₄₅ spectrum was distorted by the O-KL₂₃L₂₃, as shown in Figure 2.

It was impossible to measure the intensity of Cr-L₃M₂₃M₂₃ directly because of the influence of the O-KL₂₃L₂₃ peak. The intensity of Cr-L₃M₂₃M₂₃ was calculated from those of Cr-L₃M₂₃M₄₅ and Cr-L₃M₂₃M₄₅ by comparing the three intensities of Cr-L₃M₂₃M₂₃, Cr-L₃M₂₃M₄₅ and Cr-L₃M₄₅M₄₅ obtained from pure Cr solid. The intensity is proportional to the product of two local DOS according to the equation(1). For example,

$$I(\text{pureCr} - L_3 M_{23} M_{45}) = CN(\text{pureCr} - M_{23})N(\text{pureCr} - M_{45}) \quad (2)$$

where $I(X)$ is the intensity of X transition, $N(X)$ the number of electrons in X state, and C is the characteristic coefficient for the Auger transition process. The intensity of Cr-L₃M₂₃M₂₃ was therefore able to be calculated by

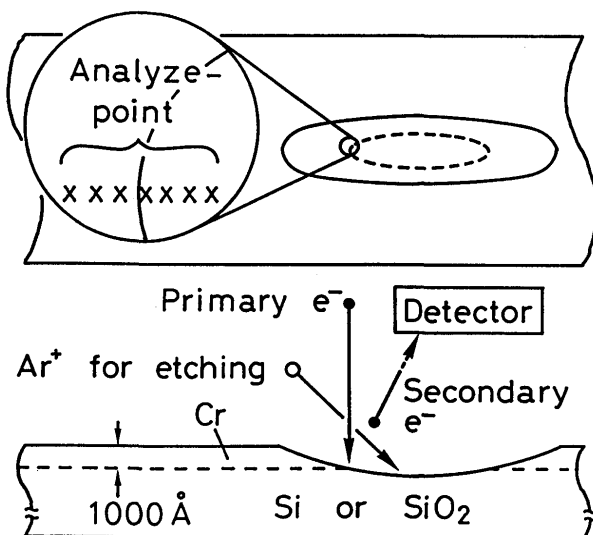


Fig. 2 Schematic illustration of Auger peaks. The intensity of Cr-L₃M₂₃M₂₃ peak is estimated as a width at x.

$$I(\text{Cr} - L_3 M_{23} M_{23}) = I(\text{pureCr} - L_3 M_{23} M_{23}) \times \frac{I(\text{Cr} - L_3 M_{23} M_{45})}{I(\text{pureCr} - L_3 M_{23} M_{45})} \times \frac{I(\text{Cr} - L_3 M_{45} M_{45})}{I(\text{pureCr} - L_3 M_{45} M_{45})} \quad (3)$$

The intensity of O-KL₂₃L₂₃ was estimated by subtracting the calculated peak of Cr-L₃M₂₃M₂₃ from the spectra. The concentration of each element was determined by the intensities of Cr-L₃M₂₃M₂₃, O-KL₂₃L₂₃ and Si-KL₂₃L₂₃ according to ref.[20].

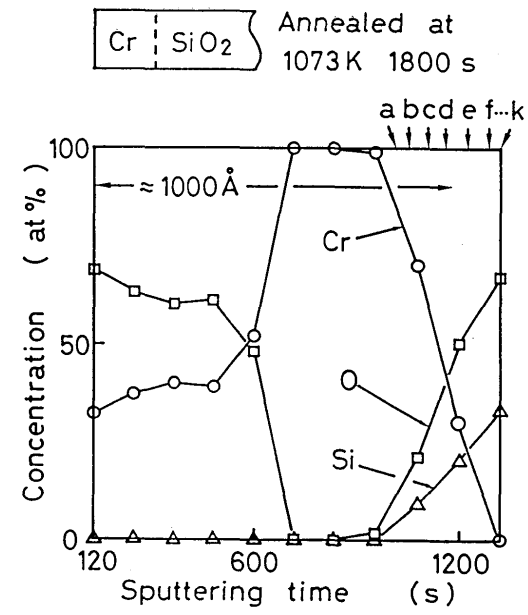
4. Results

Figure 3 shows depth profiles and Auger spectra for Cr/SiO₂ interface. Fig.3(a) is divided into three regions by sputtering time, i.e., 120 to 720s, 720 to 840s and 840s to the end. The 120 to 720s region corresponds to the surface oxidation during annealing. There exists no influence of Cr oxidation at the other two regions. The region of 720 to 840s corresponds to pure Cr, and that of 840s to the end is the broadened interface of Cr/SiO₂. There seems to be no reaction layers such as stoichiometric CrSi in the broadened interface from our depth profiles. Auger spectra involving the valence band are measured in the interface region marked with a to k. They are shown in Fig.3(b).

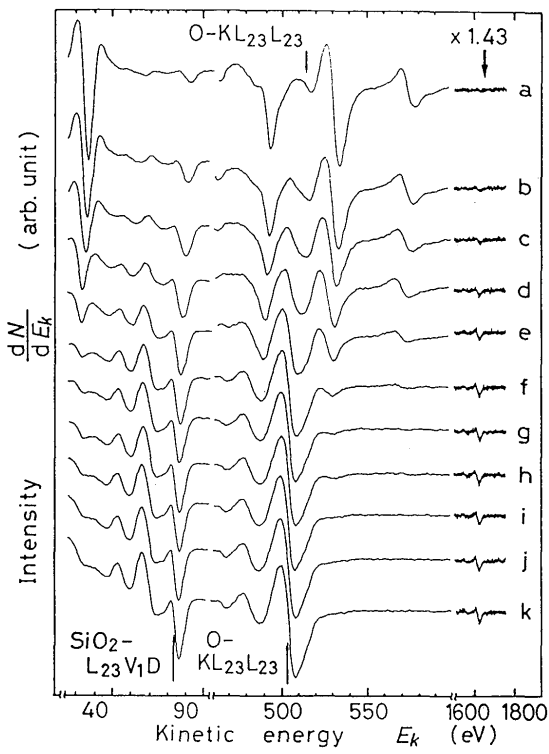
Each spectrum in Fig.3(b) shows the peaks from O-KL₂₃L₂₃ transition. The different energies correspond to the change in oxygen bonding from the Cr atom to the Si atom through the interface. The spectrum k also has a SiO₂-L₂₃V₁D peak involving the surface defect states of SiO₂. The intensity of this peak depends on the irradiation time of the primary electron, even if Ar⁺ etching was conducted on the SiO₂ surface. This peak is therefore attributed to irradiation by the primary electrons¹⁴). This result suggests that the Ar⁺ etching doesn't alter the electronic structure, in contrast to the electron beam. We, however, dared to irradiate the primary electron for a somewhat long period (640s) because we needed accurate value of Auger intensity.

Figure 4 shows depth profiles and Auger spectra for Cr/Si interface in the same manner. The spectra a and b in Fig.4(b) are influenced by surface oxidation. A reaction layer is formed in the region e. This is a chromium silicide layer on the basis of stoichiometry (Fig.4(a)). Si atoms have a stable chemical bonding with Cr atoms in this region. The region from f to h corresponds to the solid solution of Cr and Si. The region of i is the pure Si solid. As can be seen in

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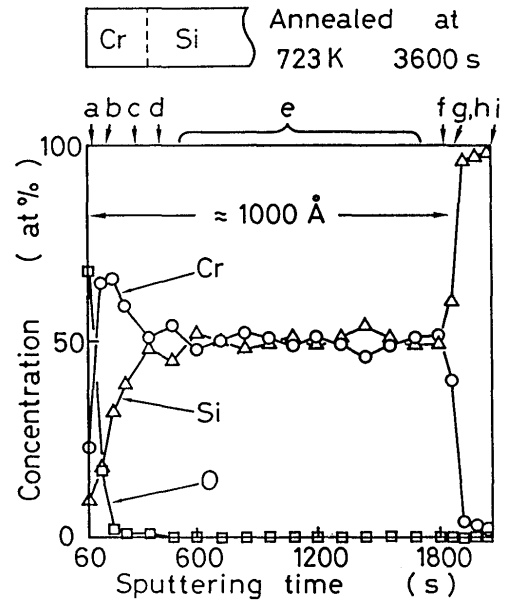


(a)

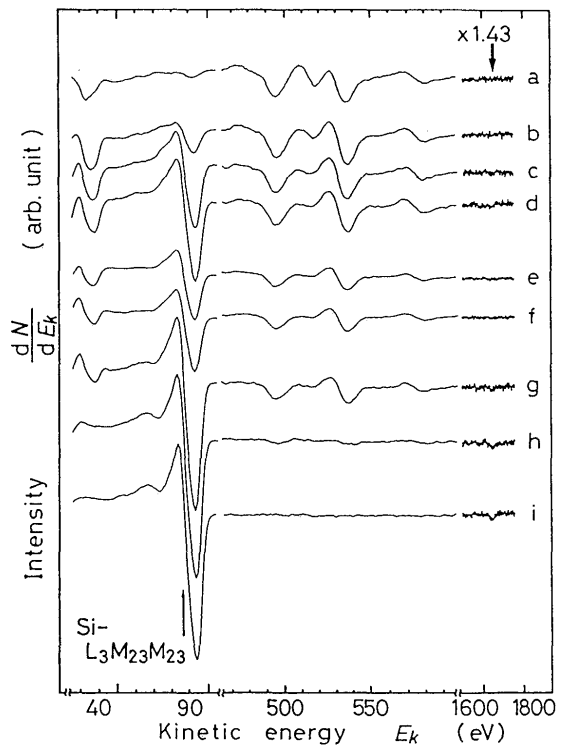


(b)

Fig. 3 The results of AES for the Cr/SiO₂ interface. (a)Concentration depth profiles. (b)Auger spectra. The Auger spectra marked with a~k in (b) correspond to the positions, a~k, in (a).



(a)



(b)

Fig. 4 The results of AES for Cr/Si interface. (a)Concentration depth profiles. (b)Auger spectra. The Auger spectra marked with a~i in (b) are respectively for the positions, a~i, in (a).

Fig.4(b), the spectra e to i exhibit the $\text{Si-L}_3\text{M}_{23}\text{M}_{23}$ peaks at the same kinetic energy, while Si atoms change in chemical bonding from Cr to Si. This suggests that the valence level for the Si-Cr bond is close to that of the Si-Si bond. This contrasts with the Si-O bond seen in Fig.3(b). The energy of $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$ peak is about 20eV lower than that of the $\text{Si-L}_3\text{M}_{23}\text{M}_{23}$ peak. This indicates that the valence level of the Si-O bond is about 10eV deeper than that of the Si-Si bond^{8,21}.

Figure 5 shows the variation of the ratio of O to Si in atomic concentration with an increase of chromium. This was a result determined from the spectra of Fig.3(b). In the region I, the ratio is kept constant in spite of the increase of Cr, and the value is two. A minimum ratio is around 50%Cr, although Fig.5 has an error. The error is very sensitive to the intensity of $\text{Si-KL}_{23}\text{L}_{23}$, but such a minimum was reproduced in this study. The minimum in the region II implies a local lack of oxygen for bonding with Si, i.e. the sp³ hybrid orbitals of Si are free from oxygen. It is inferred that there exist Cr-Si bonds in region II. In region III, the ratio is increasing with Cr content. This means that the O atom more rapidly diffuses into the Cr film than the Si atom. The minimum point in region II is produced by the rapid diffusion for the chemical bonding across the interface. This is discussed in detail in the following section.

5. Discussion

We can observe the change in the chemical bonding across the interface by measuring Auger spectra. We

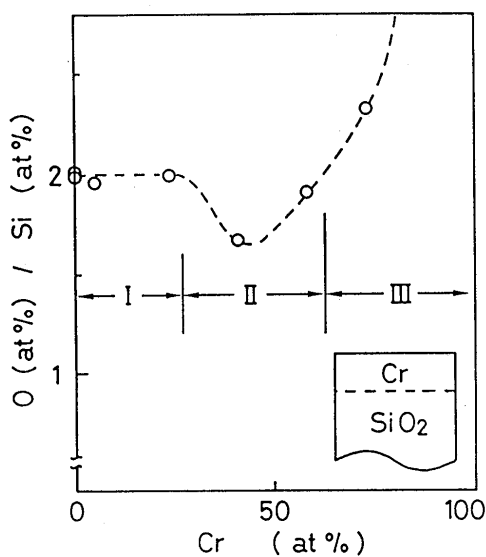


Fig. 5 Variation of the concentration ratio (O/Si) across the Cr/SiO₂ interface. Full scale of Cr from 0 to 100at% is comparable to the distance of about 300Å.

should note that the Auger spectra are from the local area, including many atoms. Therefore, we should not compare the different spectra to each other using the absolute values of the Auger intensities because they depend on the number of atoms. We have to adopt the intensity ratio of appropriate Auger peaks in the same spectrum. If we select the appropriate transitions and take their intensity ratio, then we can recognize the change in the local DOS for a particular atom.

Let us discuss the chemical bonding in a certain area at the interface of Cr/SiO₂, which is exposed to an ideal vacuum. It is suggested from the results that there are Si-O bonds, Si-dangling bonds and Si-Cr bonds, at least in this area. Si-O bonds cause the peak of $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$ transition. Si-dangling bonds are responsible for the $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{D}$ peak¹⁴. Si-Cr bonds exhibit the peak at the same position for $\text{Si-L}_3\text{M}_{23}\text{M}_{23}$ transition because the Si-Cr bond is roughly equal to the Si-Si bond with respect to the energy of the valence band, as indicated in Fig.4(b). It is naturally expected that the number of Si-Cr bonds increases when Cr increases across the interface. The number of Si-O bonds decreases with increasing Cr. Thus, we take the intensity ratio of $\text{Si-L}_3\text{M}_{23}\text{M}_{23}/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$. According to equation 2, this is comparable to the ratio of the square of the number of electrons in the Si-Cr bonding states to that of the Si-O bonding states. Moreover, this can be regarded as a value per one atom of Si. This means the probability of the Si-O and Si-Cr bond per one atom of Si. Unfortunately, we must take the ratio of $(\text{SiO}_2\text{-L}_{23}\text{V}_1\text{D} + \text{Si-L}_3\text{M}_{23}\text{M}_{23})/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$ because the $\text{Si-L}_3\text{M}_{23}\text{M}_{23}$ peak overlaps with the $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{D}$ peak as shown in Fig.3(b). The Auger intensity from $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{D}$ reflects the product of occupied V₁ states and occupied D states in number of electrons. The Auger intensity from $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$ reflects the square of V₁ states. Thus, the term of $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{D}/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$ is equivalent to the ratio of the defect states (D) to the Si-O bonding states (V₁) in number of electrons. This term $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{D}/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$ is independent of Cr content because it is mainly due to the irradiation of the primary electron (the irradiation period is kept constant for each spectrum (640s)).

Figure 6 shows that the Auger intensity ratio increases with the increase of Cr content across the interface. The value at Cr = 0% is due to the term of $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{D}/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$, which is independent of Cr content. This term can be regarded as a background for the relationship between the $\text{Si-L}_3\text{M}_{23}\text{M}_{23}/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$ term and the Cr content. The term increasing with Cr content means a ratio of $\text{Si-L}_3\text{M}_{23}\text{M}_{23}/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$. The probability for Si-O bonds decreases but

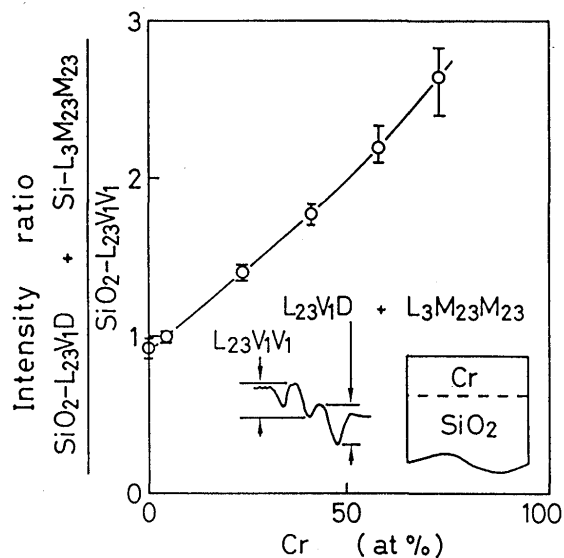


Fig. 6 Change in Auger intensity ratio with increasing Cr across the interface. The term of $\text{SiO}_2\text{-L}_{23}\text{V}_1\text{D}/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$ reflects the ratio of Si-bonds (defect states) to Si-O bonds, which is considered to be constant. The term of $\text{Si-L}_3\text{M}_{23}\text{M}_{23}/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$ reflects the square ratio of Si-Cr bonds to Si-O bonds.

that for Si-Cr bonds increases as Si atoms move toward the metal side across the interface (with respect to one atom of Si)**. This is evidence of the existence of a Si-Cr bond at the interface of Cr/SiO₂, although the reaction layer of chromium silicide is not clearly observed in the system of Cr/SiO₂.

King et al. suggested that the good adherence is a result of the chemical bonding of M(metal) and Si with O (-M-O-Si-)¹³. Pask et al. indicated the model of -M-M-O-M-O-M-O-Si-O- at the interface between metals and ceramics⁵. Our results, however, indicate the existence of an Si-Cr bond around the interface of Cr/SiO₂. Si-Cr bonds are inevitably formed from a transition of electronic structure across the interface between metals and ceramics.

The Si-Cr bond makes a new occupied DOS at the interface of Cr/SiO₂. This new DOS must exist in the band gap between SiO₂ bonding states and anti-bonding states because the Si-Cr bond is more metallic than the Si-O bond, as indicated by Fig.4(b). Figure 6 also shows that the ratio monotonically increases with increasing Cr. This means that the energy level of valence band monotonically increases with increasing Cr. As a result, the monotonical change in electronic structure is established between metals and ceramics.

** Si-Si bonds have little influence on $\text{Si-L}_3\text{M}_{23}\text{M}_{23}/\text{SiO}_2\text{-L}_{23}\text{V}_1\text{V}_1$. The authors, however, believe that the ratio is mainly due to the Si-Cr bond states because experiments show that the ratio increases with the Cr content.

According to the phase diagram²², Cr₂O₃ phase is formed at our diffused interface of Cr/SiO₂ with the thickness of 30nm. However, no Cr₂O₃ phase was observed in the present study (Fig.3(b)). The phase diagram however, is not useful to study the microstructure at the interface. The formation of a Si-Cr bond is caused by the preferential diffusion of O and Cr across the interface. Such diffusion behaviour is very important for understanding the transition of the band configuration across the interface.

Figure 7 suggests the role of oxygen for the change in the band configuration: (a) is for Cr/Si interface and (b) for Cr/SiO₂ interface. The ordinate of Fig.7 means the ratio of Cr-M₄₅ states to the Cr-M₂₃ states in number of electrons. The theory of chemical bonding tells us that the number of electrons in M₂₃ states is conservative^{23,24}. The ratio therefore reflects the occupied 3d(M₄₅) states of Cr atoms. Three marks of a, d and e in Fig.7(a) are comparable to those of Fig.4, respectively. Fig.4(a) indicates that the spectrum of a is affected by an O atom from the surface oxidation. The ratio (Cr-L₃M₄₅M₄₅/Cr-L₃M₂₃M₄₅) of a is thus somewhat less than the value of 0.5 (solid line). On the other hand, both d and e are somewhat higher than the solid line of 0.5. This can be understood by seeing Fig.4(a). The CrSi phase may be formed at the interface of Cr/Si. This silicide is responsible for the deviation of d and e above the solid line in Fig.7. The chemical bonding at the phase becomes more stable by an increase of Cr-3d electrons. However, we can say that the Cr-M₄₅ state is kept roughly constant in number of electrons instead of an increase of Si atoms.

In contrast, Fig.7(b) shows that the electrons in Cr 3d state monotonically decrease with increasing O content. This indicates that the probability for the formation of a Cr-O bond increases with Cr content; that is, molecular orbitals (MO) are produced between O and Cr, and the electrons in this MO incline toward oxygen. This is due to the large electronegativity of oxygen^{8,25}. As seen in Fig.7(b), the monotonical decrease of the ratio with increasing oxygen means that the energy level of the valence band monotonically decreases with increasing oxygen.

We should remember again that oxygen more preferentially diffuses into the Cr film than silicon. Cr-O bonds are more easily formed than Cr-Si bonds in the metal side of the Cr/SiO₂ interface. The Cr-O bonds in the metal side locally reduce the valence level of the metal (Cr)⁸. This is the role of oxygen for the bonding of metals to ceramics. On the other hand, both Cr-O bonds and Cr-Si bonds are formed in the substrate (ceramic) side. These bonds locally raise the valence level of the SiO₂ solid.

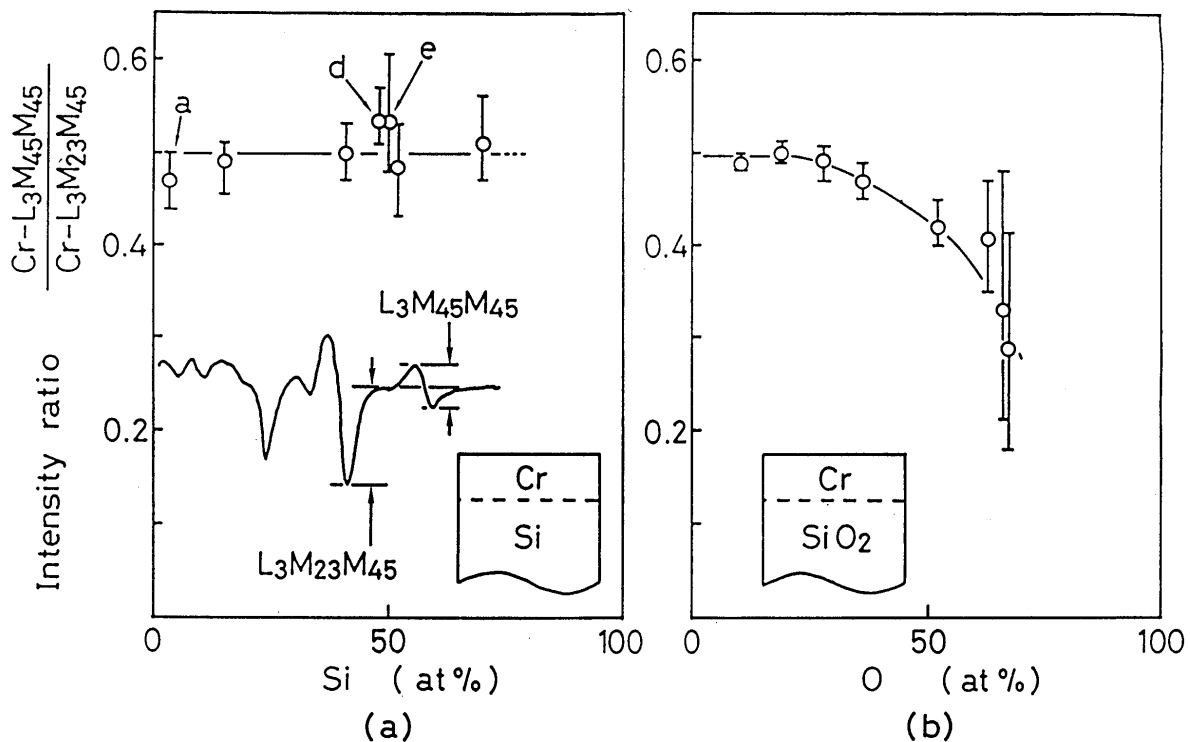


Fig.7 Change in Auger intensity ratio across the interface. The ordinate reflects the occupied Cr-3d(M_{45}) states. (a)Cr/Si interface. (b) Cr/SiO₂ interface.

6. Conclusion

By using the appropriate intensity ratio of valence Auger spectra, chemical bonding across the annealed interface of Cr/SiO₂ has been analyzed and the transition of band configuration has been studied. The main results are as follows:

- (1) No silicide layers such as CrSi are formed at the interface of Cr/SiO₂, while the silicide layer of CrSi is observed at the interface of Cr/Si.
- (2) Oxygen diffuses through the interface of Cr/SiO₂ more rapidly than silicon.
- (3) Intensity ratio of Si-L₃M₂₃M₂₃/SiO₂-L₂₃V₁V₁ monotonically increases with increasing Cr across the interface of Cr/SiO₂.
- (4) Intensity ratio of Cr-L₃M₄₅M₄₅/Cr-L₃M₂₃M₄₅ monotonically decreases with increasing O across the interface of Cr/SiO₂.
- (5) Si-Cr bonds exist at the interface of Cr/SiO₂, although silicide layers are not observed. The formation of a Si-Cr bond is due to the preferential diffusion of oxygen.
- (6) An energy shift of O-KL₂₃L₂₃ Auger peak is observed. The shift reflects the change in oxygen bonding from a Cr atom to an Si atom through the interface.
- (7) Cr-O bonds formed in the metal side of the Cr/SiO₂ interface contribute to the reduction of the valence level of Cr.
- (8) The role of oxygen is to achieve the monotonical change in electronic structure from that of an insulator (SiO₂) to that of a conductor (Cr) and to produce the tight joining between the two.

Acknowledgment

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