

# ESCA study on the mechanism of adherence of metal to silica glass

HIROKI OHNO\*, TOSHIHIRO ICHIKAWA, NOBUHIRO SHIOKAWA†, SHOZO INO, HIROSHI IWASAKI

*The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai 980, Japan*

Indium oxide films formed on the surface of silica glass samples by selective oxidation have been shown to greatly improve the adherence of gold-indium alloy to the silica glass. In order to clarify the role that the oxide films play in the reaction, thin indium films have been evaporated onto silica glass and heated at temperatures of between 973 and 1473 K, both in air and in hydrogen gas. Electron spectroscopy for chemical analysis (ESCA) measurements have then been made to investigate the chemical environments around oxygen and indium atoms at the reacting interface between the oxide and glass. Measured O1s and In3d<sub>5/2</sub> spectra reveal the formation of non-bridging oxygen atoms at the interface, in addition to the original bridging oxygen atoms in silica glass. Introduction of the non-bridging oxygen atoms and indium ions into the silica glass is concluded to be an essential factor in promoting good adherence between the gold alloy and silica glass.

## 1. Introduction

Much progress has been achieved in the study of the wetting and adherence of metal to glass and it has become clear that oxide films formed on the metal surface play a significant role in obtaining a good wetting and adherence between metal and glass. For example, an indium oxide film formed on gold-based dental alloys improves the adherence between the alloy and dental porcelains (SiO<sub>2</sub>: 69 wt%, Al<sub>2</sub>O<sub>3</sub>: 15 wt%, K<sub>2</sub>O: 11 wt%, Na<sub>2</sub>O: 5 wt%) [1]. The understanding of the origin of adherence is a very important subject from fundamental and practical points of view. There have been, however, few investigations which reveal the mechanism of the reaction between the two materials on an atomic scale. As the reaction layer is known to be of submicrometre thickness [2, 3], a probe which can give information from such a thin layer is indispensable. It is also desirable to employ an instrument which can detect a change in the chemical environment of atoms in that

layer. Electron spectroscopy for chemical analysis (ESCA) is an experimental technique most suitable for these purposes.

The aim of the present work was to obtain an understanding of the elemental mechanism of the adherence and an experimental investigation has been carried out on a simplified system of gold-indium alloy and silica glass. Chemical shifts in the binding energy of core electrons of oxygen and indium atoms have been measured by ESCA and the mechanism by which the indium oxide chemically reacts on the silica glass has been studied in some detail.

## 2. Experimental procedure

Silica glass obtained (from Toshiba Ceramics Co. Ltd) with a purity better than 99.99% was used. Spectroscopic analysis showed the presence of the following impurities; Al<sub>2</sub>O<sub>3</sub>: 40 ppm, Fe<sub>2</sub>O<sub>3</sub>: 2 ppm, Na<sub>2</sub>O: 2 ppm, K<sub>2</sub>O: 1 ppm, Cu: 0.1 ppm and B: 0.1 ppm. The Au-1 wt% In alloy

\*Present address: School of Dentistry, Higashi-Nippon-Gakuen University, Ishikari-Tobetsu, Hokkaido 061-02, Japan.

†Present address: School of Dentistry, Niigata University, Niigata 951, Japan.

was prepared by melting weighed amounts of gold (99.99% pure) and indium (99.99% pure) in argon gas using a graphite crucible. To eliminate segregation the ingot was repeatedly inverted and remelted.

In order to investigate the effect of oxide formation on the adherence of metal to glass, the gold alloy was melted at a temperature of 1373 K on the silica glass either in vacuum or in hydrogen gas. A sessile drop of the gold alloy formed on the silica glass was drawn mechanically apart to measure the strength of the adherence between the two substances.

An interfacial reaction of these substances was further studied by ESCA on the system of the silica glass and indium metal. Silica glass specimens (of dimensions 15 mm × 6 mm × 2 mm) were successively washed in acetone and boiled in ethyl alcohol and distilled water to remove surface contamination. Thin films of indium of thicknesses 10, 30 and 50 nm were evaporated onto the silica glass in a vacuum of  $10^{-4}$  Pa. The In-covered silica glasses were heated in air and in hydrogen gas for 30 min at temperatures ranging from 973 K to 1473 K. The hydrogen gas was successively dried by passing through sulfuric acid, silica gel and phosphorus pentoxide to eliminate water vapour.

ESCA measurements were performed using an AEI-ES 200 electron spectrometer using  $AlK\alpha$  radiation (1486.6 eV). Instrumental resolution was estimated from the width of the Au  $4f_{7/2}$  peak to be 1.3 eV\*. The spectrometer was evacuated to between 0.7 and  $2.7 \times 10^{-6}$  Pa, by oil diffusion pumps with cold traps, during the measurement. Binding energies of measured photoelectron peaks were calibrated by using the C1s peak of hydrocarbon contamination at a binding energy of  $285.0 \pm 0.2$  eV. The In-covered silica glass and standard materials were heated for 1 h at 473 K in the spectrometer before the measurement in order to desorb water molecules on the specimen surface. The binding energy of the C1s peak of the hydrocarbon contamination changes to values near that of the C1s peak of graphite by heating at temperatures above about 600 K in the spectrometer [4], which is presumably due to contamination of the graphite by carbonization of the hydrocarbon. However, this change does not occur on heating at lower temperatures. Hence the C1s peak can be

used as a standard for binding energy even after heating at 473 K. The specimens were irradiated by X-rays for 1 h and then the measurement of photoelectron peaks was initiated. This process was necessary to avoid a complicated shift of photoelectron peaks caused by a change in the charging of the specimens. The shift resulting from the charging was checked by measuring the C1s peak before and after the measurement.

A conventional scanning electron microscope was employed to make a morphological observation of the reacting surfaces.

### 3. Experimental results

#### 3.1. Adherence of Au–In alloy to silica glass

A small sample of the Au–In alloy was heated for 30 min at 1373 K on the silica glass either in hydrogen gas or in an ultra-high vacuum of pressure about  $10^{-6}$  Pa in order to try to form a chemical reaction between the alloy and the silica glass. In these atmospheres, the alloy became a sessile drop on the silica glass, but an indium oxide layer was not formed on the surface of the alloy. When the drop was lightly pulled away from surface, at room temperature after the heating, it was easily torn from the glass without any trace being left on the glass surface, as shown in Fig. 1a. This indicates that the reaction did not occur and the drop was simply in contact with the silica glass without any adherence.

Next, another alloy sample was heated in an ordinary high vacuum of  $\sim 10^{-4}$  Pa for 30 min. This heat treatment produced a thin oxide layer on the surface of the alloy. The sessile drop formed adhered so tightly to the silica glass that it could not easily be torn away from the glass. When the pulling force was increased, fracture occurred inside the glass, as shown in Fig. 1b, revealing that the strength of the adherence is larger than the bonding force in the silica glass itself.

When the alloy was heated in air, heavy oxidation occurred and a thick oxide layer was formed on the surface before melting. This layer prevented the alloy from forming the sessile drop and prevented good contact between the alloy and silica glass. This led to a poor adherence, though trace of the reaction was seen at some positions of the glass surface where the alloy was in contact with the silica glass.

These results of the sessile drop test clearly

\*1 eV =  $0.16022 \times 10^{-18}$  J

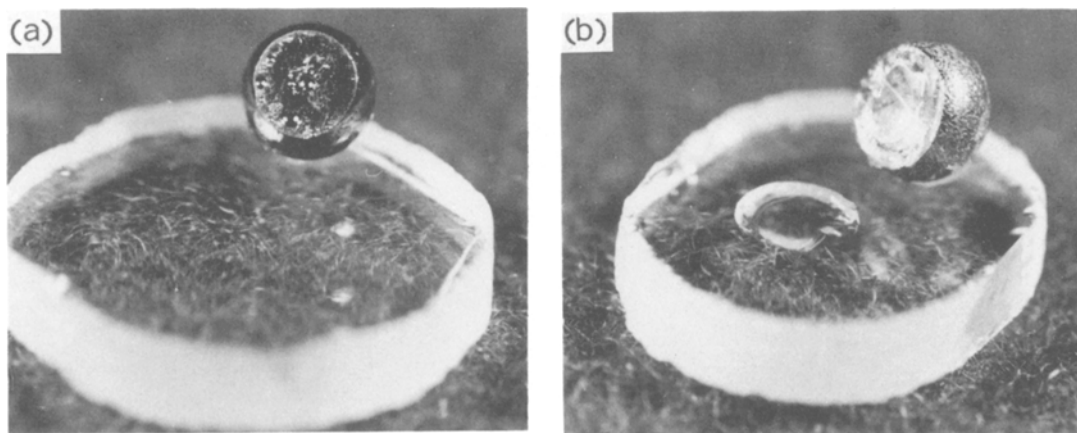


Figure 1 Sessile drop-test of Au-In alloy on silica glass after heating (a) in hydrogen gas and (b) in vacuum,  $10^{-4}$  Pa.

show that the existence of a thin oxide layer at the interface between the gold alloy and silica glass is necessary for the adherence between the two substances.

### 3.2. ESCA O1s spectra of silica glass and $\text{In}_2\text{O}_3$

Fig. 2 shows the O1s spectra obtained from clean silica glass and bulk  $\text{In}_2\text{O}_3$  (99.9% purity), both of which served as standard materials. The spectra for the silica glass shows a symmetrical peak at 532.6 eV. Silicon atoms in the glass are known to be linked tetrahedrally to the neighbouring four oxygen atoms, while the oxygen atoms are linked

to the two adjacent silicon atoms by covalent bonds [5]. Hereafter, we shall call such oxygen atoms "bridging oxygen atoms". On the other hand, the O1s spectrum of  $\text{In}_2\text{O}_3$  has an asymmetrical peak at 529.6 eV. Oxygen atoms in  $\text{In}_2\text{O}_3$  are ionized to form the  $\text{O}^{2-}$  state. The shoulder on the higher binding energy side of the peak became lower after heating at 473 K in the spectrometer. The lowering indicates that the shoulder is due to remaining adsorbates such as water and oxygen molecules.

### 3.3. ESCA O1s spectra obtained from the In-covered silica glass heated in air

After indium films, of thickness 10, 30 and 50 nm, were evaporated onto silica glasses, they were heated at 973 K for 30 min in air so as to allow the reaction of the indium film with the glass to take place. An attempt to heat the samples in an ordinary high vacuum of  $\sim 10^{-3}$  Pa was unsuccessful, because a rapid desorption of In atoms occurred and the deposited In was entirely lost before a measurable amount of the reacting layer was formed. Fig. 3 shows a set of O1s spectra obtained from the three specimens heated in air. The peak positions of the O1s spectra from the silica glass and  $\text{In}_2\text{O}_3$  standards are indicated by the symbols  $\text{O}_B$  and  $\text{O}^{2-}$  in Fig. 3, respectively. A peak in Spectrum a in Fig. 3 lies at a binding energy near to that of the  $\text{O}^{2-}$  state of  $\text{In}_2\text{O}_3$ . A shoulder is seen on the high binding energy side of the peak. With decreasing thickness of the indium film, the peak shifts slightly to a larger binding energy position and the shoulder develops to the well-shaped peak.

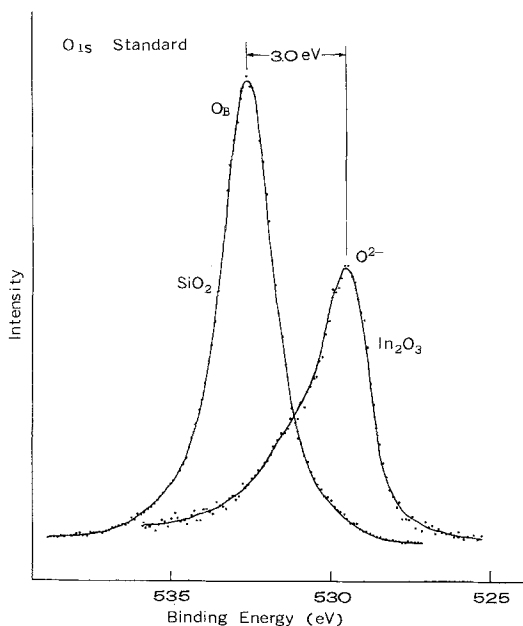


Figure 2 O1s spectra of clean silica glass and bulk  $\text{In}_2\text{O}_3$ .

Figs 4 and 5 show the O1s spectra obtained

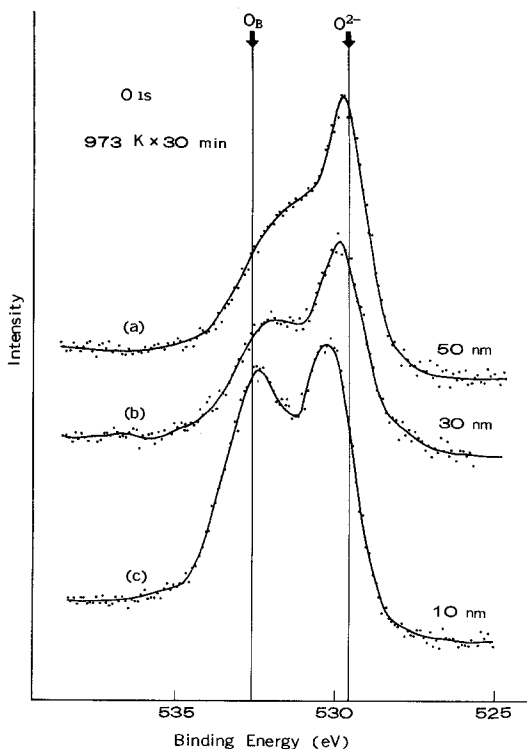


Figure 3 O1s spectra measured from the In-covered silica glass heated at 973 K for 30 min in air. Thickness of indium films is (a) 50 nm, (b) 30 nm and (c) 10 nm.  $O_B$  and  $O^{2-}$  indicate the peak positions arising from the bridging oxygen atoms and divalent oxygen anions, respectively.

from the specimens heated at 1173 K and 1373 K for 30 min, respectively. The spectra have two peaks with a difference in binding energy of between 2.0 and 2.2 eV. The peak at higher binding energy in these figures is larger for the specimen with thinner indium film, as seen also in Fig. 3. The O1s spectra shown in Figs 3, 4 and 5 also show that, for the specimens with indium films of the same thicknesses, the peak on the higher binding energy side increases in intensity with increasing temperature. Since the peak positions in Spectrum b and Spectrum c in Fig. 5 almost coincide with the  $O_B$  position, the peak is attributed to the bridging oxygen atoms; the peak at lower binding energy in Fig. 5 is not due to the  $O^{2-}$  state, because any kind of superposition of the two standard spectra shown in Fig. 2 cannot give rise to that peak at the intermediate binding energy. In order to determine the binding energy of the peak, the  $O_B$  peak is subtracted from the measured spectrum, as shown in Fig. 6, assuming that the peak due to the bridging oxygen atom has the same shape as that shown in Fig. 2. The

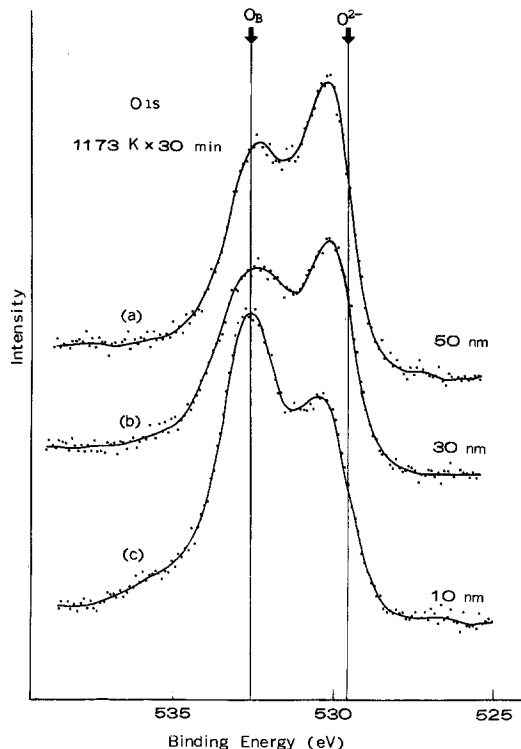


Figure 4 O1s spectra measured from the specimens heated at 1173 K for 30 min in air.

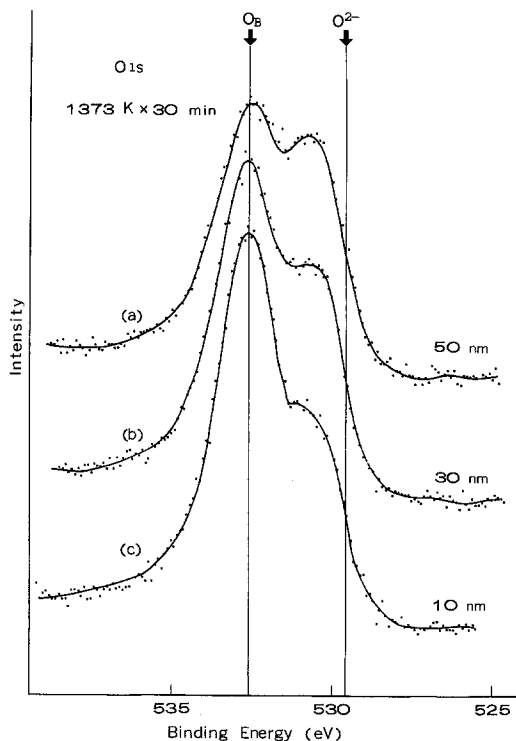


Figure 5 O1s spectra measured from the specimens heated at 1373 K for 30 min in air.

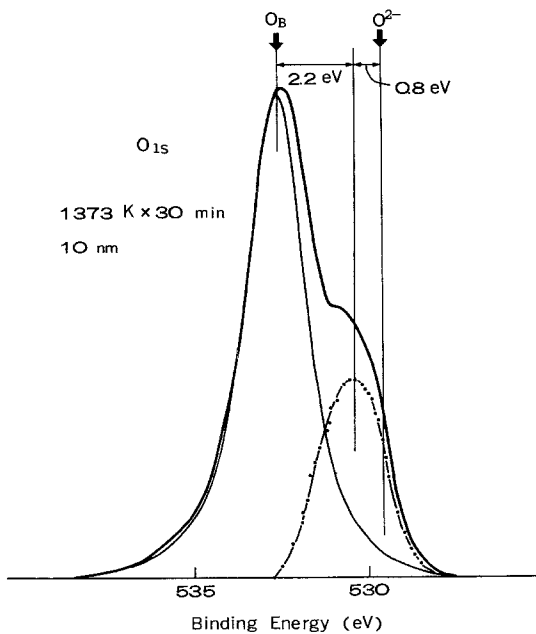


Figure 6 Decomposition of the O1s spectrum from the specimen (In film 50 nm) heated at 1373 K for 30 min. The decomposed peak at lower binding energy is attributed to a new state of oxygen atoms produced by high temperature reaction of indium film and silica glass.

resultant spectrum has a peak at a binding energy of 530.4 eV, higher by 0.8 eV than that of O<sup>2-</sup>. The interpretation of the O1s spectra in Figs 3 and 4 will be given later.

The possibility must be examined that the peak at 530.4 eV might be due to the adsorbed water molecules remaining on the surface. In order to determine the binding energy of the O1s peak of the adsorbed water, an In-covered silica glass, from which the O1s spectrum, Spectrum c in Fig. 4, was obtained, was exposed to water vapour and the O1s spectra from the specimen were measured before and after heating for 1 h at 473 K. Both spectra and the difference between them is shown in Fig. 7. The difference ( $\Delta I$ ) gives a new peak at a binding energy that is lower by about 0.5 eV than that of the bridging oxygen (O<sub>B</sub>), but this peak does not coincide with the peak in the resultant spectrum exhibited in Fig. 6.

Fig. 8 shows the relation between the heating temperature and the binding energy of the In3d<sub>5/2</sub> core electrons measured from the specimens with the 50 nm thick indium film. The binding energy for the specimens heated at 973 K coincides with

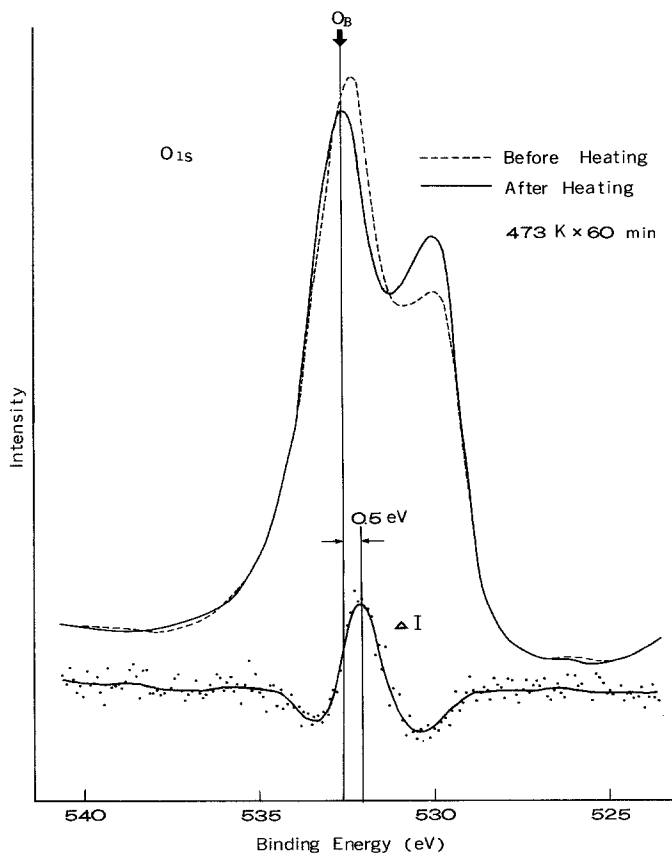
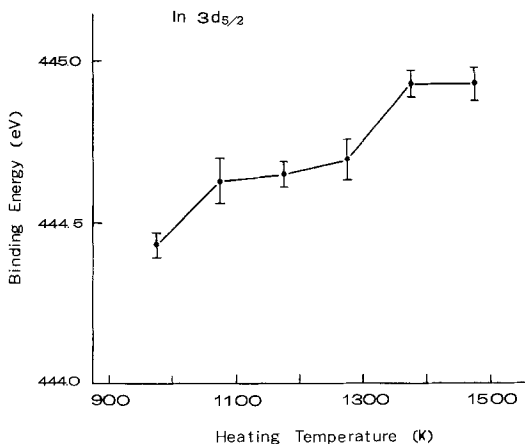


Figure 7 O1s spectra from a specimen, which was exposed to water vapour for a short time, before (broken line) and after (solid line) heating at 473 K for 1 h in the spectrometer, and their difference spectrum.



**Figure 8** Binding energy of indium  $3d_{5/2}$  core electrons from the specimens heated at various temperatures for 30 min in air. The indium film on the silica glass was 50 nm thick before heating.

that of  $\text{In}3d_{5/2}$  obtained from the bulk  $\text{In}_2\text{O}_3$ , i.e. that of the  $\text{In}^{3+}$  state, 444.3 eV. The  $\text{In}3d_{5/2}$  binding energy shifts to higher values with increasing temperature. The shift suggests that the reaction of  $\text{In}_2\text{O}_3$  and silica glass at high temperatures changed indium atoms from the  $\text{In}^{3+}$  ionic state to some other chemical state.

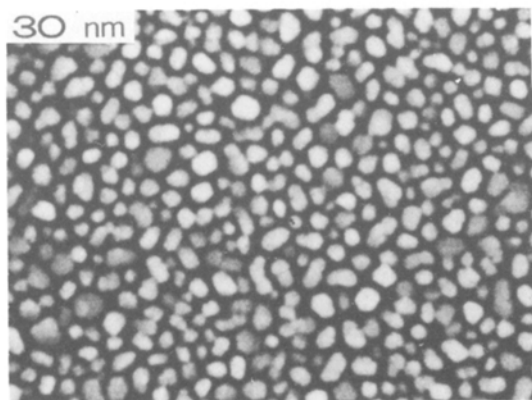
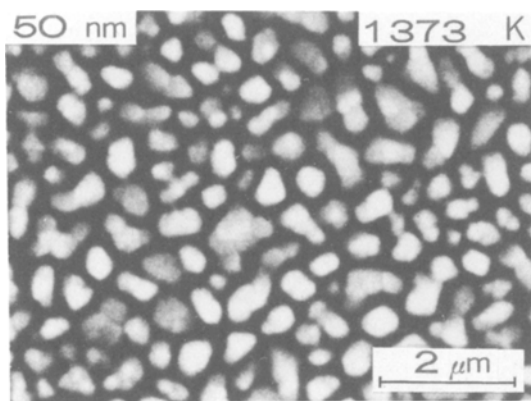


Fig. 9 shows a set of scanning electron microscope images of the specimen surfaces heated at 1373 K. The thicknesses of the In films were 10, 30 and 50 nm, respectively. These images consist of bright patches or islands of irregular shape. This feature is quite different from that of the images obtained from the specimens not heat-treated, which show structureless contrast. The size of the islands depends remarkably on the thickness of the evaporated indium films and increases with increasing thickness. Such a feature was also observed for the specimens heated at lower (937 K) and higher (1473 K) temperatures.

### 3.4. ESCA spectra obtained from the In-covered silica glass heated in hydrogen gas

Fig. 10 exhibits an O1s spectrum obtained from the specimen heated at 1073 K for 30 min in hydrogen gas, Spectrum b, together with that obtained from the specimen heated in air, Spectrum a. The peak in Spectrum b is sharp and symmetrical except for a small shoulder on the low binding energy side. The binding energy and width of the symmetrical peak are equal to those of the peak obtained from the clean silica glass. A small peak which comes from the shoulder remains after subtracting the symmetrical peak from the measured spectrum. Its binding energy is found to be 529.7 eV, which can be correlated with that of the peak of the  $\text{O}^{2-}$  state, within experimental error. The peak at 530.4 eV in the O1s spectrum,

**Figure 9** Scanning electron microscope images of the specimen surfaces heated at 1373 K for 30 min in air. Indium films of thickness 50, 30 and 10 nm were evaporated onto the respective silica glass samples before heating.

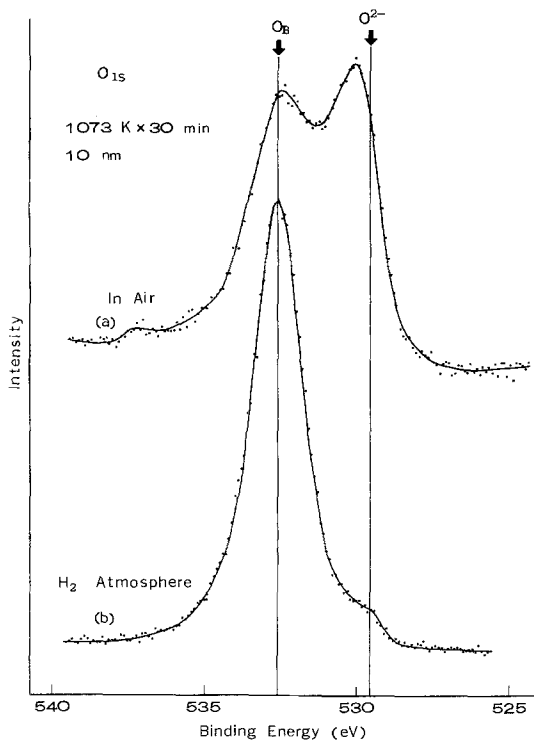


Figure 10 O 1s spectra measured from the specimens heated at 1073 K for 30 min (a) in air and (b) in hydrogen gas. The specimens were covered with an indium film of thickness 10 nm before heating.

Spectrum a, of the specimen heated in air is not seen in the spectrum from the specimen heated in hydrogen gas.

Fig. 11 shows a scanning electron microscope image from the specimen from which the O 1s spectrum, Spectrum b in Fig. 10, was obtained. Bright round particles are seen in the image, which

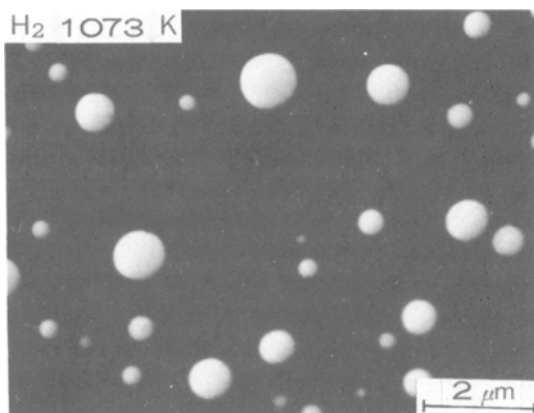


Figure 11 Scanning electron microscope image of specimen surface heated at 1073 K for 30 min in hydrogen gas. Indium film was 10 nm thick before heating.

are quite different in shape from those seen in Fig. 9. The round shape suggests that indium was in a liquid state during heating at 1073 K and did not react on the silica glass surface at all. When the specimen was transferred from the furnace to the spectrometer after heating in the hydrogen gas, the surface of the particles was naturally oxidized and an extremely thin  $\text{In}_2\text{O}_3$  layer was formed. The small shoulder shown in Spectrum b in Fig. 10 is due to this  $\text{In}_2\text{O}_3$  layer.

## 4. Discussion

### 4.1. Reaction of deposited indium film and silica glass at high temperature

The ESCA experiment on the specimen heated in hydrogen gas revealed that indium atoms in a metallic state in contact with silica glass did not react with the silica glass even at temperatures as high as 1073 K. On the other hand, when the indium films are oxidized by heating in air, they rapidly react in contact with the silica glass. These observations elucidate that the reaction occurring between the deposited indium film and the silica glass is really a chemical reaction of  $\text{In}_2\text{O}_3$  and silica glass. The reaction noticeably changes the shape of the O 1s spectra of the In-covered silica glasses, as shown in Figs 3, 4 and 5. The O 1s spectrum, Spectrum c in Fig. 5 shows that the new peak lies on the low binding energy side of the  $\text{O}_B$  peak. The  $\text{O}_B$  peak arises from the bridging oxygen atoms in the silica glass. The new peak at a binding energy of 530.4 eV, which is about 2.2 eV lower than that of the  $\text{O}_B$  peak, indicates that a new state of oxygen atoms is generated at the reacting interface. Several kinds of adsorption species such as water, oxygen molecules and hydroxyl ions are present on the glass surface exposed to air [6–8] and their O 1s spectra may superpose on the measured O 1s spectra. The peak due to the adsorbed water is clearly different in energy from the new peak, as shown in Fig. 7. If the other species were responsible for the new peak, it would not be possible to explain such systematic changes of the O 1s spectra with changing film thickness and reaction temperature, as seen in Figs 3, 4 and 5. Therefore, the appearance of the new peak is entirely due to the high temperature reaction of silica glass and  $\text{In}_2\text{O}_3$ .

Anderson [9] and Brückner *et al.* [10, 11] reported that O 1s spectra of sodium silicate glasses have a pronounced shoulder on the low binding energy side of the  $\text{O}_B$  peak and the intensity of

the shoulder increases as the soda content increases. They attributed the shoulder to the non-bridging oxygen atoms which are linked with one silicon atom and one sodium ion. According to their measurement, the difference between the O1s binding energies of the bridging and non-bridging oxygen atoms is 1.8 to 2.0 eV. Kaneko *et al.* [12] measured the O1s binding energy of various orthosilicates such as  $2M \cdot \text{SiO}_2$  (where  $M = \text{Ca}, \text{Ni}, \text{Mn}, \text{Mg}, \text{Li}, \text{Zn}, \text{Be}$  or  $\text{Sn}$ ) in which oxygen atoms are in the non-bridging state. Their binding energies are lower by 0.8 to 2.0 eV than that of the  $\text{O}_B$  peak in silica glass. The lower binding energy was also reported by Yin *et al.* [13], Huntress *et al.* [14], Tossell [15] and Kaneko [16]. By analogy with differences in O1s binding energies observed in the previous works, it is concluded that the new peak at 530.4 eV, shown in Fig. 6, is attributed to the non-bridging oxygen atoms which are bonded with one silicon atom and to neighbouring indium ions by ionic bonds.

Fig. 12 is a schematic representation of the local atomic environment around the non-bridging oxygen atoms, showing the state of the bonding. In Fig. 12 the indium ions are surrounded by non-bridging oxygen atoms and are in a new chemical state different from that in  $\text{In}_2\text{O}_3$ . Since changes of atomic environment around an atom modify the potential acting on the core electrons, through variations in the distribution of valence

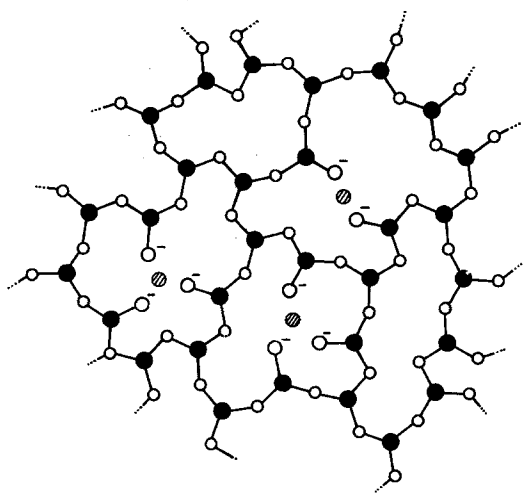


Figure 12 Local atomic environment around non-bridging oxygen atoms and dissolved indium ions in silica glass. Closed, open and hatched circles represent silicon atoms, oxygen atoms and indium ions, respectively.

electrons, and cause a shift in the binding energy of the core electron, this new environment of indium atoms will be responsible for the shift of the  $\text{In}3d_{5/2}$  binding energy, as shown in Fig. 8.

Now, a reaction process is depicted in order to explain the systematic changes in the O1s spectra shown in Figs 3, 4 and 5. When the In-covered silica glass is heated in air, the indium film melts to form small round drops on the glass and simultaneously begins to oxidize to  $\text{In}_2\text{O}_3$ . The patches or islands in the scanning electron microscope images of Fig. 9 are vestiges of the drops. On further heating, the drops completely oxidize and the glass surface is covered with an  $\text{In}_2\text{O}_3$  layer. The O1s spectrum measured from these specimens is nothing else other than that of  $\text{In}_2\text{O}_3$  because the  $\text{In}_2\text{O}_3$  layer is much thicker than the escape depth of the O1s photoelectrons. When the specimens are heated at temperatures above 973 K, a chemical reaction takes place at the interface between the  $\text{In}_2\text{O}_3$  layer and silica glass, and the indium and oxygen ions begin to dissolve in the silica glass, being associated with the formation of the non-bridging oxygen atoms. As the reaction proceeds, the amount of  $\text{In}_2\text{O}_3$  becomes so small that the reacting interface is exposed. Consequently, the O1s photoelectron peaks from the bridging and non-bridging oxygen atoms at the interface can be detected by ESCA.

The O1s spectrum, Spectrum a in Fig. 3, has a peak near the  $\text{O}^{2-}$  position and its shape is similar to that of the O1s spectrum of the standard  $\text{In}_2\text{O}_3$ , though the shoulder on the high binding energy side of the peak is undetectable in the latter spectrum. This means that a considerable amount of  $\text{In}_2\text{O}_3$  still remains unreacted on the surface. The reaction time until the  $\text{In}_2\text{O}_3$  layer is completely reacted will decrease with decreasing thickness of the indium films and increasing reaction temperature; as the indium film becomes thinner and the reaction temperature becomes higher the remaining amount of  $\text{In}_2\text{O}_3$  on the surface decreases, resulting in an increase in the intensity of the O1s photoelectron peaks arising from the bridging and non-bridging oxygen atoms. In the O1s spectrum (Spectrum b in Fig. 3) from the silica glass with 30 nm thick indium film the increase causes the shift of the peak and the development of the shoulder. On the surfaces covered with a thinner indium film and heated at a higher temperature the reacting interface reaches the surface and the  $\text{In}_2\text{O}_3$  layer does not remain. The two peaks in



the O1s spectra from these surfaces shown in Spectrum c in Fig. 3 and in Spectra a and b in Fig. 4, are attributed to the bridging and non-bridging oxygen atoms.

As the reaction proceeds, the dissolved indium ions and the non-bridging oxygen atoms diffuse from the surface region to the interior of the silica glass and cannot be probed by ESCA. Consequently the densities of the dissolved indium ions and the non-bridging oxygen atoms decrease in the surface region. The decrease leads to a reduction of the non-bridging oxygen peak height. This is in a good agreement with what can be seen in a series of the O1s spectra, Spectra b and c in Fig. 4 and Spectra a, b and c in Fig. 5.

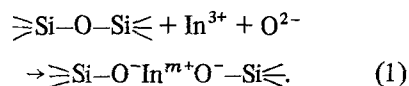
On the other hand, when the In-covered silica glass is heated in hydrogen gas, the indium film melts to small round drops but indium oxide is not formed on the surface. On heating, neighbouring drops coalesce to form larger drops and a wide area of the glass surface is exposed. As indium metal atoms cannot dissolve in the silica glass, the drops lie in the glass surface, remaining unreacted during heating. When the specimen is transferred from the furnace to the spectrometer after heating the surface of the drops is oxidized. Hence, the spectrum measured from the specimen heated in hydrogen gas is a superposition of spectra from silica glass and  $\text{In}_2\text{O}_3$ . This explains Spectrum b in Fig. 10.

#### 4.2. Mechanism of the adherence of gold–indium alloy to silica glass

The sessile drop test clearly showed that a thin oxide layer of indium on the Au–In alloy plays an indispensable role in making a strong adherence of the alloy to silica glass. In the test, the adherence was made by heating in a high vacuum, but not in an ultra-high vacuum. This might be seen as an unreliable result, because the total pressures of residual gases in both the vacuums are low by comparison with those in air. However, since the partial pressure of water vapour, which is an important factor promoting the oxidation of indium metal, is greatly reduced in the ultra-high vacuum by baking out the vacuum chamber of the furnace thoroughly, the conclusion is considered to be reasonable.

When the oxide is heated on the glass at a high enough temperature, the oxide dissolves in the silica glass and breaks the covalent bond which links the silicon and oxygen atoms. This results in

the destruction of the random network of  $\text{SiO}_4$  tetrahedra in the silica glass, generating the non-bridging oxygen atoms. An oxygen ion is necessary for an indium ion to dissolve in the silica glass, as can be seen from the relation:



Since the valency of the indium ions dissolved in the silica glass is not determined in the present work, the valency is denoted as an unknown value,  $m$ , in Equation 1; the oxygen ion will be supplied from the indium oxide layer.

A transition layer containing a number of the non-bridging oxygen atoms is formed near the interface between the indium oxide layer and the silica glass by the dissolution of indium and oxygen ions. Previous studies [2, 17] have pointed out that an excellent adherence does not develop until all the oxide layer dissolves and vanishes. When the oxide layer existing between the Au–In alloy and silica glass completely dissolves in the silica glass by the reaction, the indium ions linked with the non-bridging oxygen atoms will come into direct contact with metal atoms at the interface between the transition layer and the alloy and chemical bonds will be formed with the metal

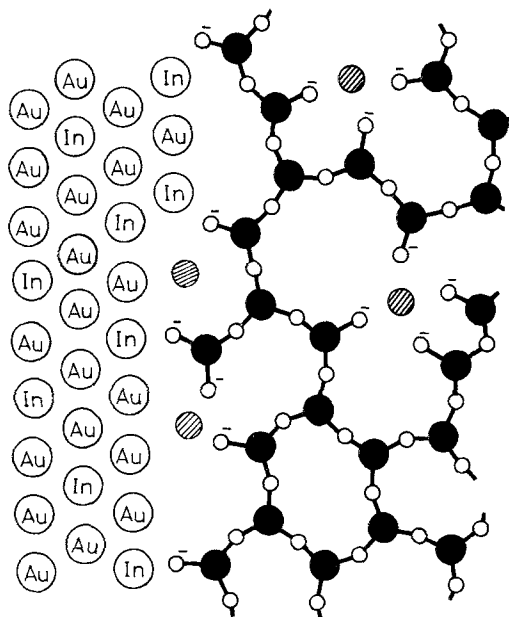


Figure 13 A sketch of structure near the interface between the Au–In alloy and the silica glass. Closed, open and hatched circles represent silicon atoms, oxygen atoms and indium ions respectively.

atoms. The Au–In alloy and silica glass are thus tightly bonded. Fig. 13 is a sketch of the structure near the interface.

In summary, the introduction of the non-bridging oxygen atoms and indium ions into the silica glass is concluded, from the present sessile drop test and ESCA measurements, to be an essential factor in the making of a good adherence of the Au–In alloy to silica glass.

### Acknowledgements

The authors wish to thank Mr Y. Kaneko and Drs M. Oku and K. Asami for their helpful advice on ESCA measurement and also Dr A. Ohkawa for the use of a heating equipment in a hydrogen gas atmosphere. This work has been supported by a fund of the Japan Council for Promoting Sciences.

### References

1. J. W. McLEAN and I. R. SCWD, *Trans. Brit. Ceram. Soc.* **72** (1973) 235.
2. B. W. KING, H. P. TRIPP and W. H. DUCKWORTH, *J. Amer. Ceram. Soc.* **42** (1959) 504.

3. D. E. CLARK, C. G. PANTANO and G. Y. ONADA, *J. Amer. Ceram. Soc.* **58** (1975) 336.
4. K. HIROKAWA, F. HONDA and M. OKU, *J. Electron Spectrosc.* **6** (1975) 333.
5. B. E. WARREN, *J. App. Phys.* **8** (1937) 645.
6. J. M. THOMAS and M. J. TRICKER, *J. Chem. Soc. Faraday Trans., II* **71** (1975) 329.
7. C. R. BRUNDLE, T. J. CHUANG and K. WANDEL, *Surface Sci.* **68** (1977) 459.
8. D. L. PERRY, D. W. BONNELL, G. D. PARKS and J. L. MARGRAVE, *High Temp. Sci.* **9** (1977) 85.
9. P. R. ANDERSON, Proceedings of the Meeting of the American Chemical Society, New York (1973).
10. R. BRÜCKNER, H. U. CHUN and H. GORETZKI, *Glastechn. Ber.* **49** (1976) 211.
11. *Idem, ibid.* **51** (1978) 1.
12. Y. KANEKO and Y. SUGINOHARA, *J. Japan Inst. Metals* **41** (1977) 375.
13. L. I. YIN, *Science* **173** (1971) 633.
14. W. T. HUNTRESS, *Earth Planet. Sci. Lett.* **15** (1972) 59.
15. J. A. TOSSELL, *J. Phys. Chem. Sol.* **34** (1973) 307.
16. Y. KANEKO, *Yogyo-Kyokai-Shi* **86** (1978) 38.
17. J. BERK, *J. Amer. Ceram. Soc.* **41** (1958) 287.

Received 15 October and accepted 21 November 1980.