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STUDY OF THE Al/GRAPHITE INTERFACE*

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Thin Al films with a thickness of 20–30nm were prepared by ultra-high vacuum deposition of Al onto a graphite surface parallel to a (0001) basal plane. The samples were annealed up to 1070K. X-ray photoelectron spectroscopy analysis has shown that for temperatures just higher than 770K, a little carbide occurs in the Al film and only an Al–C phase is present at the Al/graphite interface. After annealing at 970K, the Al_4C_3 phase can be observed, and the binding energy of the Al2p electrons increases continuously from 72.7 to 74.2eV with increasing temperature up to 1070K. Auger electron spectroscopy depth profiles are measured to investigate the phases existing in the Al film as well as at the Al/graphite interface. It is found that the Al_4C_3 phase at the interface is the final product of a series of Al carbides from the interfacial reaction between Al and graphite.

Keywords: aluminium, graphite, interface
PACC: 6822, 6848, 7960

I. INTRODUCTION

The Al–C system is an important binary system. Al_4C_3 carbide is now known as the only intermediate compound in the system. The thermodynamic properties and stability of Al_4C_3 have been reported in the literature.[1−3] In our study on the Al/TiC interface,[4,5] it is found that the Al_4C_3 carbide phase occurs at the interfacial region due to the chemical interactions between aluminium and the carbon in TiC at temperatures higher than 1020K. The presence of this phase at the interface is undesirable because it is weak and brittle. In order to clarify the interaction mechanism of metal Al with carbon, we have designed an experiment for investigating the interfacial phenomena of the Al–C binary system. The purpose of the present study is to characterize the chemical states of Al and C in the Al/graphite interface at different temperatures between 770 and 1070K using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

II. EXPERIMENTAL DETAILS

The samples investigated in this study were prepared by evaporating aluminium (purity higher than 99.9%) onto the cleaved pyrolytic graphite surface, which is parallel to the (0001) basal plane. The thickness of the Al films was in the range between 20–30nm. Prior to depositing metal Al, the graphite substrates were heated to 900K in the evaporation chamber to remove contamination, and verified by subsequent XPS analysis. During evaporation, the pressure in the vacuum chamber remained below 1.6×10^{-7}Pa. The growth rate of the Al films was 5nm/min. Annealing experiments were performed at temperatures ranging from 770 to 1070K. All XPS photoelectron spectra were measured in ESCA MKII, using a Mg $K\alpha$ source ($E_{K\alpha}$=1253.6eV). Binding energies (B.E.) were calibrated with the $4f_{7/2}$ peak of a clean Au surface at 84.0eV,[6] and the C1s peak at 284.2eV of high-purity pyrolytic graphite.[7] The AES experiment was carried out on a Perkin–Elmer Model PHI-610 scanning Auger microprobe. Auger depth profiling was performed with 2.0kV Ar^+ ions incident at an angle 45° with respect to the sample normal, by alternately acquiring data and sputtering.

III. RESULTS AND DISCUSSION

Figure 1 shows the Al2p and C1s core-level photoelectron spectra obtained by means of XPS. In the C1s spectra, the peaks related to the graphitic and carbidic phases are well separated and at fixed bind-

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ing energies. For the as-deposited sample, the C1s peak position is at 284.4eV, close to the binding energy of the C1s of high-purity graphite (284.2eV).[7] After annealing, a new C1s peak appears at 281.4eV, indicating an Al–C carbide forms by interdiffusion of C and Al, which might be the Al_4C_3 phase as observed by Lu *et al.*[4] using X-ray diffraction (XRD). In contrast, the Al2p spectra show that with an increasing annealing temperature, a new peak at the high binding energy side gradually develops, which corresponds to the carbidic Al. This carbidic Al2p peak shifts continuously to higher binding energies with a maximum shift of 1.5eV with respect to the metallic Al2p peak (72.7eV). Moreover, a peak broadening from 1.0eV full width at half-maximum (FWHM) at room temperature to a value of 1.3eV at 970K is found. Above 970K, the carbidic Al2p peak position remains at 74.2eV; however, we can observe the change of the peak intensity, indicating that the reaction of Al with graphite at the surface might have completed.

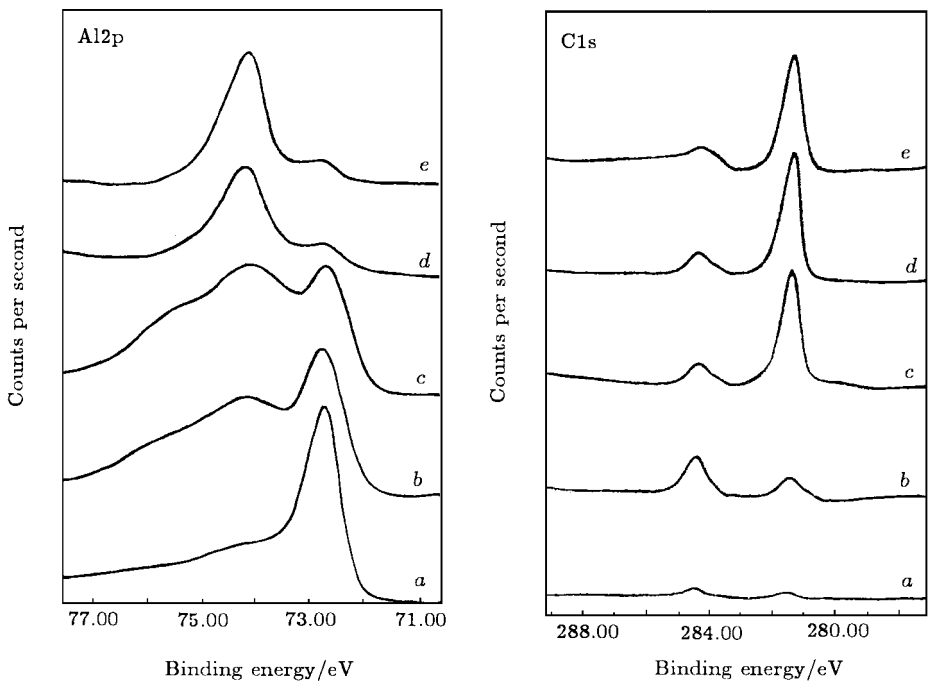


Fig.1. Al2p and C1s core level photoelectron spectra of the samples as-deposited (*a*) and annealed at temperatures of 770K (*b*), 870K (*c*), 970K (*d*) and 1070K (*e*).

The C1s spectra show no obvious changes in intensity of the carbidic peak above 970K. These observations indicate that there is a transition through an Al–C interfacial region at an intermediate temperature until a well-defined Al_4C_3 phase forms at 1070K. To investigate the entire interface, Auger depth profiles were performed with an as-deposited sample, as well as the samples annealed at the temperatures shown in Fig.2. The profile of the as-deposited sample (Fig.2(a)) shows that there is no obvious evidence of a chemical reaction between the Al layer and graphite substrate, only an interdiffusion region is formed at the interface. However, for the sample annealed at 770K (Fig.2(b)), the AES depth profile shows that the relative concentrations at the surface are 9at% of graphitic C, 83at% of pure Al and a small amount (≈2at%) of carbidic C. With increasing depth, the carbidic C concentration increases to a maximum value of ≈13at%. Such a result may be due to either the presence of a small amount of Al_4C_3 within the Al layer, or the incident interfacial reaction during the heat treatment. The carbidic C concentration is always lower than that of Al in the entire interface studied.

The graphitic C concentration in the Al film is more than that expected from the solubility of graphitic C in Al, according to the equilibrium phase diagram.[3] Deeper into the substrate where the Al concentration is low, no unreacted Al but the carbidic Al can be detected. It is also worth noting that there is no evidence for the presence of oxygen at the interface between the metal Al layer and the graphite (0001) substrate. This indicates that the native oxide is effectively removed by the surface treatment. The Auger depth profile of a sample annealed at 970K

(Fig.2(c)) shows a maximum carbidic C concentration of ≈45at% in the Al/graphite interface, which approaches a stoichiometric carbon concentration in Al_4C_3 (≈43at%). Also, the corresponding XPS spectra show that Al has reacted with graphite to form an Al carbide phase. For this sample, the XPS spectra recorded after each sputtering also show a shift of the Al2p peak up to 74.2eV. With an increasing annealing temperature up to 1070K (see Fig.2(d)), the highest carbidic C concentration in the interfacial region remains unchanged.

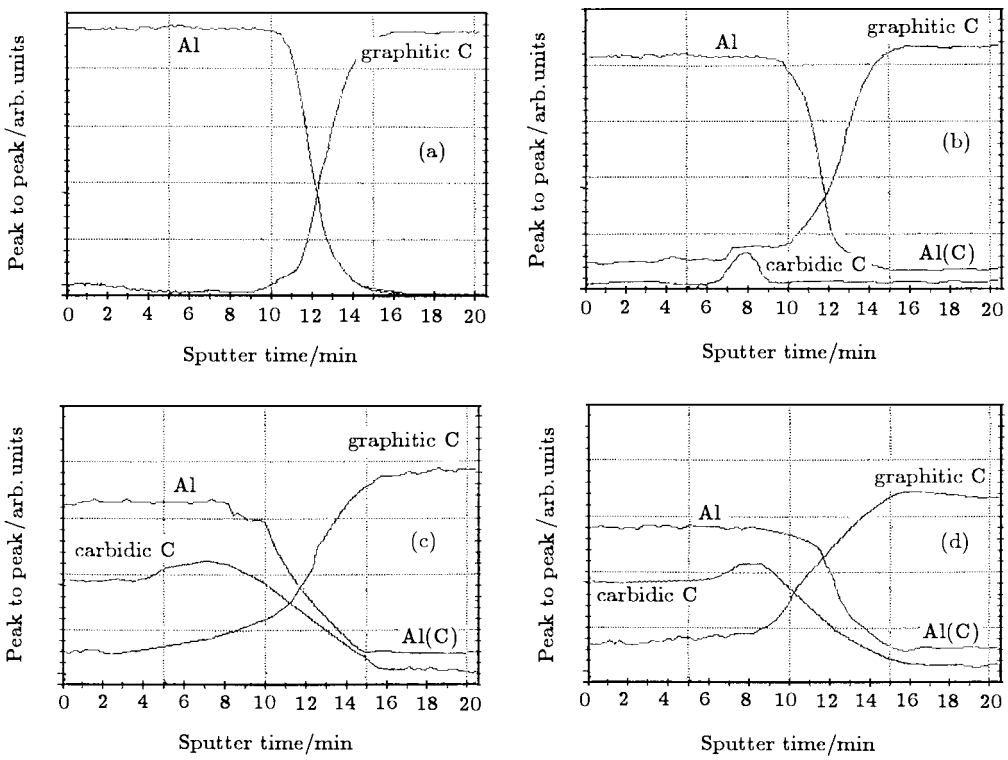


Fig.2. Auger depth profiles for the samples as-deposited (a) and annealed at 770K (b), 970K (c) and 1070K (d).

Based on the Al–C phase diagram,[3] it can be seen that, for all temperatures at which we carried out studies, the coexistence of liquid Al and solid carbon requires the existence of an intermediate phase Al_4C_3. For this reason, for this system at equilibrium, it is impossible to directly dissolve solid carbon into liquid Al unless the temperature is above the melting point of Al_4C_3. Our experimental results show that the interfacial reactions between Al and the graphite (0001) plane also include a dynamic or quantum-chemistry process, such as interfacial diffusion, electron transition and chemical bonding, etc. Moreover, we believe that a phase transition temperature exists, above which a carbidic phase, Al_4C_3, can form. The carbide Al_4C_3 is now known as the only stable intermediate compound in the Al–C binary system. This kind of carbide is very brittle at the ambient temperature, as indicated by Lee *et al.*[8] and Iseki *et al.*[9] so that Al_4C_3 can be susceptible to some ambient vapours, such as H_2O, CH_3OH, HCl etc. Qiu *et al.*[3] have examined the stability of Al_4C_3 through thermodynamic calculations under various conditions. It has been shown that the standard Gibbs energy for the Al_4C_3 formation at 298.15K is –194.4 kJ/mol, and its formation enthalpy is –206.9 kJ/mol. Considering that the free energy of the Al/graphite interface decreases at high temperatures due to the increase of entropy, we believe that the following reaction is tenable: $4\ Al+3C \longrightarrow Al_4C_3$. Because the reaction may depend strongly on temperature, a series of intermediate products, such as AlC, AlC_2, Al_2C_2 and Al_4C_3 may form at the interface by diffusion and reaction of Al with graphite. However, only a stable phase Al_4C_3 has now been identified at the Al/graphite interface by XPS and AES.

IV. CONCLUSION

According to the experimental results obtained in the Al–C binary system from XPS and AES analyses, the interfacial reaction between Al and the graphite substrate occurs at temperatures higher than 770K, and one of the major reaction products is Al_4C_3. Our results have revealed that the brittle phase Al_4C_3 is very important for understanding the interfacial behaviour in the Al–C binary system.

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