Compositional and Chemical State Analysis of Layered Intermetallic Compounds by Line Scanning of an Etched Crater with Scanning XPS

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Abstract

Layered intermetallic compounds formed by annealing titanium film deposited on copper substrate were characterized by scanning XPS. There were three kinds of intermetallic compounds, γ-TiCu, Ti_3Cu_4 and $TiCu_3$ in the specimen. With a scanning X-ray photoelectron spectrometer, we measured the photoelectron intensities and binding energies along a line which crosses an etched crater made by ion sputtering. The intensity profile along the line by using Cu 2p3/2 for Ti-Cu layered specimen clearly showed plateaus corresponding to each compound. XPS spectra of Cu 2p3/2 at each plateau clearly showed the chemical shifts upon the formation of intermetallic compounds. The binding energy is higher in intermetallic compounds than in pure Cu. Chemical shift in Ti 2p3/2 was also observed among intermetallic compounds. Both composition and chemical state in each layer of layered material can be simultaneously characterized in situ by scanning XPS.

1. Introduction

Materials with layered structure have widely been developed for industrial use. In fabrication process of films, intermetallic compounds of non-equilibrium phases are sometimes formed. The characterization of intermetallic compounds formed at interfaces is important for material development such as metallization of semiconductor devices. By the development of XPS instruments, mapping using photoelectron peak has become possible. This ability enables us to do depth analysis of chemical state in multi-layered materials by line scanning of a crater. In this study, layered intermetallic compounds formed by annealing film deposited on substrate were characterized by a scanning XPS. The validity of line scanning of an etched crater for compositional and chemical state analysis of layered intermetallic compounds is evaluated.

2. Experimental

When Ti film(1μm thick) deposited on Cu substrate was heated at 850K for 1 hr. in a vacuum of approximately 10^{-7} Pa, three intermetallic compounds were formed. These compounds were attributed to γ-TiCu, Ti_3Cu_4 and $TiCu_3$ from X-ray diffraction patterns[1]. Ar ion accelerated at 2kV was irradiated onto specimens without raster to make a crater. The approximate depth of an etched crater was 3μm. The secondary electron image of the crater is shown in Fig.1. The line in the figure indicates the position of analysis described below. A scanning X-ray photoelectron spectrometer(PHI Quantum 2000) was used for the measurement. Al Kα X-ray was generated from a small area using a focused electron gun and is monocromatized by quartz crystals. Quartz crystals are aligned with two-dimensional curvature so that the area of X-ray generation is projected on a specimen[2]. X-ray beam of 10 μmφ in size with 20 W was used for this study. For reference, binding energies of pure Cu and Ti were also measured. The reproducibility of binding energy was within ±0.03 eV. To convert the distance in line scanning into the depth, the etched crater was traced with a stylus.

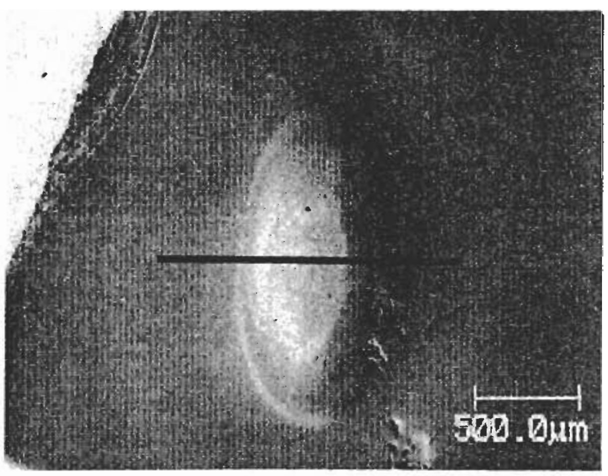

Fig. 1 Secondary electron image of an etched crater of the specimen.

3. Results and Discussion

With a scanning X-ray photoelectron spectrometer, we measured the photoelectron intensity and the binding energy along a line which crosses an etched crater. In Fig.2, an intensity profile along the line is plotted by using Cu 2p3/2 for Ti-Cu layered specimen. Each plateau is attributed to γ-TiCu, Ti_3Cu_4, $TiCu_3$, or Cu as shown in Fig.2 according to its order in intensity. Figure 3 shows the XPS spectra of Cu 2p3/2 at several points indicated in Fig.2. Chemical shifts upon the formation of intermetallic compounds are clearly seen. The binding energy is higher in intermetallic compounds than in pure Cu. The binding energy differences among intermetallic compounds are also observed. The binding energies for the layers are listed in Table 1. The XPS spectra of Ti 2p3/2 at the same points are shown in Fig.4. The binding energy in $TiCu_3$ was approximately 0.2 eV higher than those in γ-TiCu and Ti_3Cu_4. The stylus profile of the crater is shown in Fig.5 together with the intensity line profile of Cu 2p3/2. From the comparison between the stylus profile and the intensity line profile, the thickness of each intermetallic compound are estimated to be 0.3 μm for γ-TiCu, 0.7 μm for Ti_3Cu_4, and 1.2 μm for $TiCu_3$, respectively. Although the amount of error in the stylus profile is not small, a line profile of the crater made by ion sputtering will give the information about the thickness of each layer in addition to the information about composition and chemical state of each layer. It is shown that the line profiling technique with a scanning XPS enables us to analyze the composition and the chemical state of layered materials as thick as sub-micrometer.

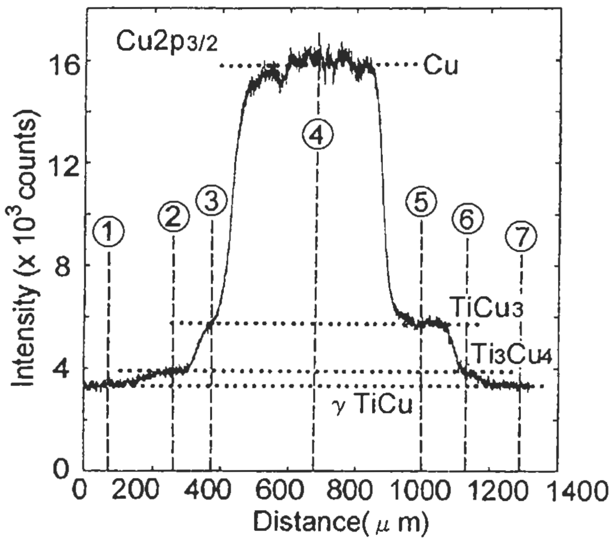

Fig. 2 An intensity profile along the line on a crater for the Ti-Cu specimen.

Table 1 Binding energy of Cu 2p3/2 in Ti-Cu specimen

layer	binding energy (eV)
Cu	932.67
$TiCu_3$	932.88
Ti_3Cu_4	933.01
γ-TiCu	933.01

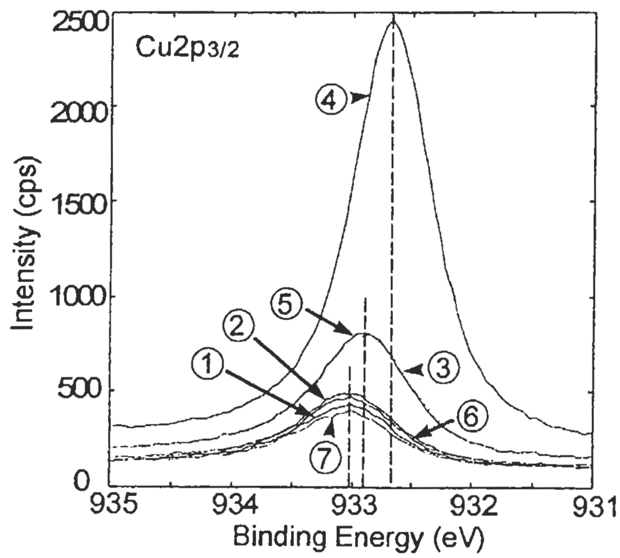

Fig. 3 XPS spectra of Cu2p3/2 at several points indicated in Fig.2.

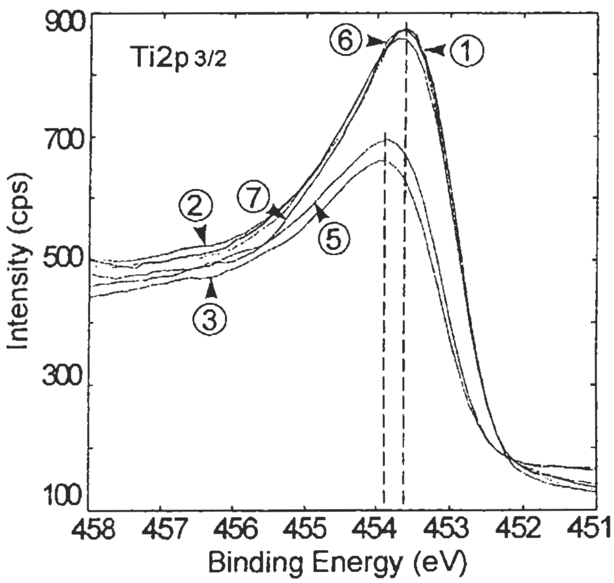

Fig. 4 XPS spectra of Ti2p3/2 at several points indicated in Fig.2.

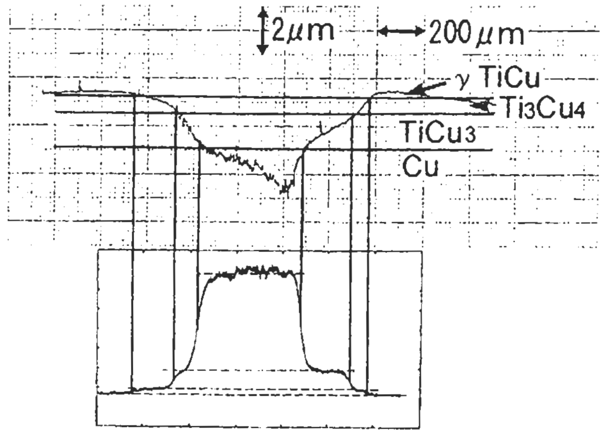

Fig. 5 A stylus profile of the etched crater with the intensity profile for the Ti-Cu specimen.

4. Conclusion

Layered intermetallic compounds formed by annealing a titanium film deposited on a copper substrate were characterized by a scanning XPS. There were three kinds of intermetallic compounds, γ-TiCu, Ti_3Cu_4 and $TiCu_3$ in the specimen. The photoelectron intensity and binding energy were measured along a line which crosses an etched crater made by ion sputtering. The intensity profile along the line by using Cu 2p3/2 clearly showed plateaus corresponding to each compound. The XPS spectra of Cu 2p3/2 at each plateau clearly showed the chemical shifts upon the formation of intermetallic compounds. The binding energy differences among intermetallic compounds are also observed. Also in XPS spectra of Ti 2p3/2, the binding energy difference among intermetallic compounds is observed. The line profiling technique with a scanning XPS enables simultaneous analysis of the composition and the chemical state of layered materials as thick as sub-micrometer.

References

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