X-ray photoelectron spectroscopic study of surface modification of SiLK * by diluted oxygen under UV-irradiation

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X-ray photoelectron spectroscopy (XPS) was used to investigate the surface modification of SiLK* resin (*Trademark of the Dow Chemical Company). SiLK* is one candidate for an ultralow-k material to be used in future integrated circuits. However, its poor adhesion to interconnection metals is a serious obstacle to practical use. Surface modification of the resin is an effective way to improve the adhesion.

In this study, 400-nm-thick SILK* films coated on Si substrates were irradiated with UV light (λ = 172 nm) in about 0.01% diluted oxygen atmosphere after vacuum pumping to modify the surface. The surface characteristics were evaluated by XPS.

Figure 1 shows XPS survey spectra of the surface layer of SiLK* films at an observation depth of less than about 5 nm. Before UV irradiation, SILK* films contain dominantly carbon and only a trace amount of oxygen; but UV irradiation markedly increases the intensity of the oxygen peaks.

Figure 2 shows XPS spectra of the C1s peak for SiLK* films (a) without irradiation and (b) after UV irradiation for 10 min. There are four main components, which previous reports have generally assigned to the various types of carbon bonds shown in the figure. Surely, the experimental result supports that a carbon atom combines with oxygen atoms after UV irradiation

Although most of the assignments are related to carbon and oxygen, the theory predicts that these four peaks can correspond to combinations of a carbon atom and another atom, molecule or group besides oxygen. And the difference in binding energy for each component is reflected in the number of carbon bonds, with more bonds corresponding to a greater binding energy. Furthermore, as shown in Fig. 2, UV irradiation does not significantly change the shape of the peaks or the ratio of the peak heights in the C1s spectra, although it does markedly increase the amount of oxygen. This probably means that UV irradiation causes a certain element or group attached to a carbon site in SiLK* to be replaced by oxygen. These results suggest the following scenario:

A carbon atom combines with a certain element or group, X, in SiLK* film, with the dominant structure being X–C=X, in which a carbon shares a single bond with one X and a double bond with another X. The precise molecular structure of SiLK* is not clear, but it is thought to be principally an aromatic hydrocarbon and that non-irradiated films contains a small amount of oxygen. The most likely candidate for X is the phenyl group (C_6H_5). UV irradiation seems to easily break the bond between carbon and X, and the active bond of carbon then combines with oxygen. It is also possible that UV irradiation generates active oxygen atoms, which act on the bond between carbon and X. O1s spectra clearly reveal that UV irradiation increases the amount of components related to combinations of oxygen and carbon.

Thus, it can be concluded that UV irradiation of the surface of SiLK* is an effective method of surface modification because it creates active carbon bonds or active oxygen atoms. It is sure that UV irradiation makes an oxidization of the thin layer of SiLK* surface even a trace of oxygen. The surface oxidation of SiLK* must improve its adhesion to metals as its surface is chemically active.

A change in the surface components of SiLK* must certainly affect how it reacts with metals. So, the surface modification of SiLK* by means of UV irradiation should be very useful in improving its adhesion to metals.

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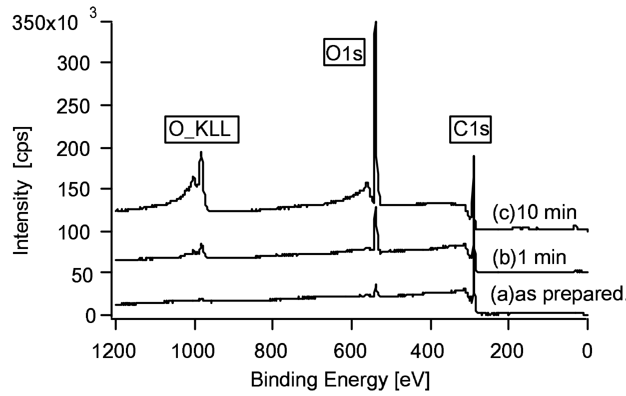

Fig. 1. XPS survey spectra for SiLK* (a) without UV irradiation, and after (b) 1 min. and (c) 10 min. of UV irradiation.

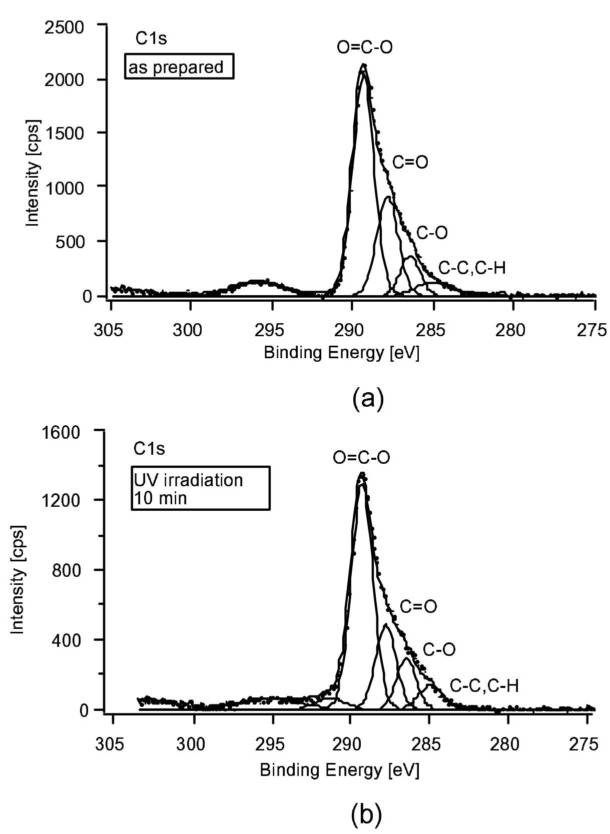

Fig. 2. XPS spectra of the C1s peak for SiLK* (a) without irradiation and (b) after UV irradiation for 10 min.