Quantized Electronic States in Metallic Nanostructures studied by Angle-resolved Photoemission Spectroscopy

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Physical properties of nanostructures of solids have attracted much interest because they are expected to differ strongly from those of the corresponding bulk crystals. In a small nanocrystallite with a size from a few nanometers to several tens of nanometers, the quantum confinement effects on the elementary excitations become predominant. In this study, angle-resolved photoemission studies for the Ag nanofilms and Ag double nanofilm structures grown on a Cu(111) substrate have been performed in order to investigate the quantized electronic states in metallic nanostructures.

Figure 1 shows the angle-resolved photoemission spectra in normal emission geometry for Ag(111) nanofilms with the thickness of 1.0-12.0 nm. The fine-structures are observed in the binding energy region corresponding to the band-structure mismatch region along Γ-L direction (surface normal direction) between Ag and Cu. As shown in Fig. 1, the binding energies of these fine-structures change systematically as a function of Ag nanofilm thickness. Therefore, it is considered that these fine-structures originate from quantum-well (QW) states due to the quantum confinement effect on Ag *sp* valence electrons. It is found that the spectral binding energy dependence on the nanofilm thickness is well characterized by the phase accumulation model which takes into account the phase shifts on the electron reflection at both interfaces of Ag nanofilm. Moreover, it is found that the QW states show the two-dimensional parabolic dispersions with the same effective mass as that of bulk Ag *sp* valence band.

A temperature-dependent photoemission study for QW states in Ag nanofilms has been performed so as to elucidate the electron-phonon coupling in Ag nanofilms. Figure 2 shows the temperature dependence of linewidths for surface state and QW states in Ag nanofilms with the thickness of 3.0 and 5.0 nm. The linear temperature dependence of the linewidths of both states are explained as the temperature dependence of the phonon contribution to the photohole lifetime width. It is found that the temperature coefficient for the electron-phonon coupling for QW states is almost the same with that for surface state and an average over the bulk Fermi surface. The temperature dependence of the photoemission intensities have been discussed using standard Debye-Waller factors. It is found that the effective Debye temperature derived from the QW state is higher than that from the surface state, suggesting different properties of phonon states coupled to each electronic state.

An angle-resolved photoemission study for Ag/Cu/Ag/Cu(111) double nanofilm structures has been performed in order to elucidate the electronic coupling between the QW states. It is found that the binding energies of QW states in Ag double nanofilm structures show an avoided-crossing behavior as a function of outer Ag nanofilm thickness, indicative of the electronic coupling between the QW states through a thin Cu barrier layer. The energy separation of the avoided-crossing is

identified with twice magnitude of the coupling matrix element between the inner and outer QW states. Figure 3 shows the dependence of the energy separation of the avoided-crossing between the inner QW state with n=1 and outer QW state with n=1 on the Cu barrier thickness. As shown in Fig. 3, the coupling strength between the inner and outer QW states decreases with increasing the Cu barrier thickness. Figure 4 shows the dependence of the energy separation of the avoided-crossing between the inner QW state with n=1 and outer QW state with n=1 on the binding energy at the avoided-crossing. As shown in Fig. 4, the coupling strength between the inner and outer QW states decreases with increasing the binding energy of the avoided-crossing relative to the Cu *sp* band edge. Moreover, it is found that the binding energies of QW states in the double Ag nanofilm structures and the dependence of the energy separation of the avoided-crossing on the Cu barrier thickness and the binding energy are well characterized by the theoretical calculation based on the nearly-free-electron approximation.

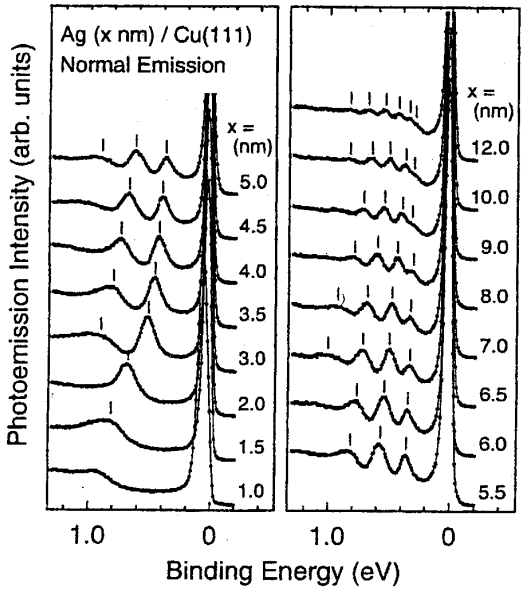

Fig. 1 Angle-resolved photoemission spectra for Ag nanofilms.

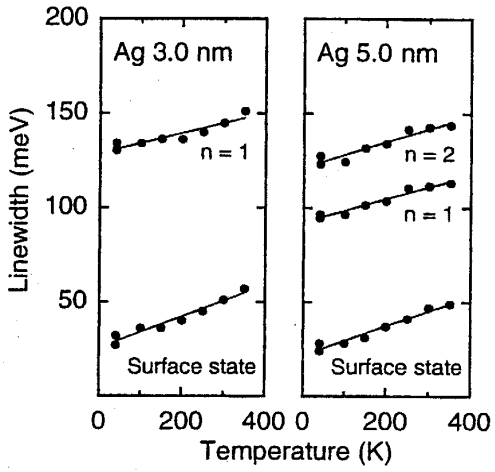

Fig. 2 Temprature dependence of the phoemission linewidths for QW states and surface state.

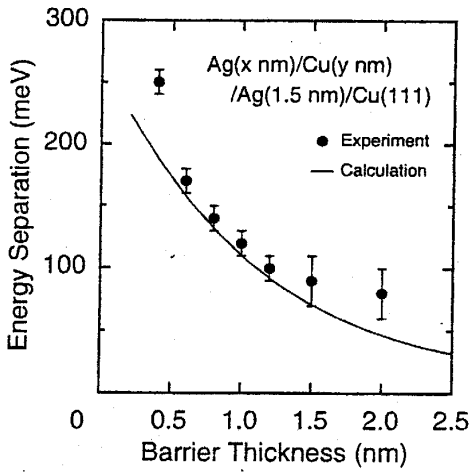

Fig. 3 The dependence of the energy separation at the avoided-crossing on the Cu barrier thickness.

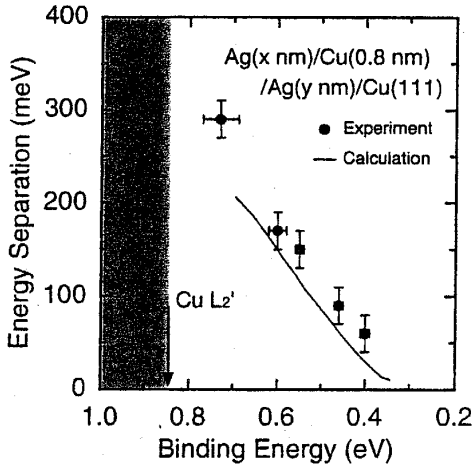

Fig. 4 The dependence of the energy separation at the avoided-crossing on the binding energy.