[III~19]

# *Surface induced phase separation in Ag-Pd Alloy*

I.S. Choi and C.N. Whang
Physics Department and Atomic Scale Surface Science Research Center
Yonsei university, Seoul, Korea
C. Hwang*
Process Characterization Group, Materials Evaluation Center
Korea Research Institute of Standards and Science, Taejon, Korea

Previous theoretical and experimental reports on Ag-Pd alloy system predict the negative heat of solution so that Ag and Pd form alloy easily. So this system has long been used to study the electronic structure of alloys in general sense. This alloy system is a disordered metallic solid solution below the melting temperature. Although the elements differ in their nuclear charge by only 1, the pure metals are chemically very different because Pd has an open d shell and Ag does not. This leads to a much higher adsorption energy of hydrogen and small molecules with unsaturated bonds on Pd, and a generally higher catalytic activity. In this letter, we will give the direct evidence on the phase separation induced by the surface in Pd-Ag alloy at room temperature. Our direct evidence comes from the high resolution study of the core-level spectra of x-ray photoelectron spectroscopy. So far, no direct observation of the surface induced phase separation in alloy system has not been observed as far as the authors are aware of.

The alloy of Pd-Ag was made by arc-melted method. After melting, one set of samples were homogenized by annealing under argon at 850$^0$C for 40 hours. Figure 1(a) shows the spectrum of Pd 3d core level using non-monochromatized Al-anode source and figure 1(b) shows the same spectrum using monochromatized source. Without the high resolution source, no one can expect the two components. Instead, one can easily regards it as an asymmetric single peak. Because the intensity of each peak varied with the ratio of the compositions, the spectra obtained with non-monochromatized source may lead to misunderstanding to the chemical state of the sample. This is the main reason why the observed core level peak shift is saturated at the finite value of the concentration. Figure 2 shows the effect of variation of the composition of Pd in $Pd_{1-c}Ag_c$. As the amount of Pd increases, the intensity of the higher binding energy peak of Pd $3d_{5/2}$ increases. The peak positions of the spectra are 335.2 eV(peak A) and 334.5 eV(peak B) and the position is not varied with the composition of alloys. The full width at half maximum of higher binding energy peak is more broad than that of lower binding energy peak, which is mainly due to the variation in conduction band electrons upon alloying.[16] The relative

concentration of the two peaks increases monotonously as the concentration of Pd increases in Pd-Ag alloys. The inset of Fig 2 is the angle dependence of Pd $3d_{5/2}$ spectra.

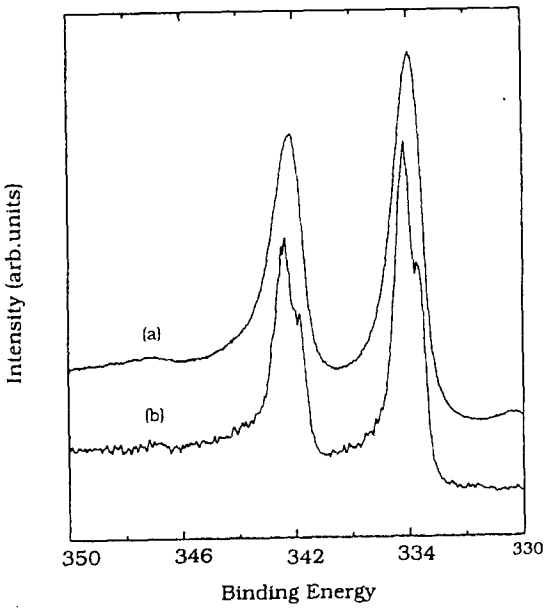


Fig 1. The Pd 3d spectra with x-ray source

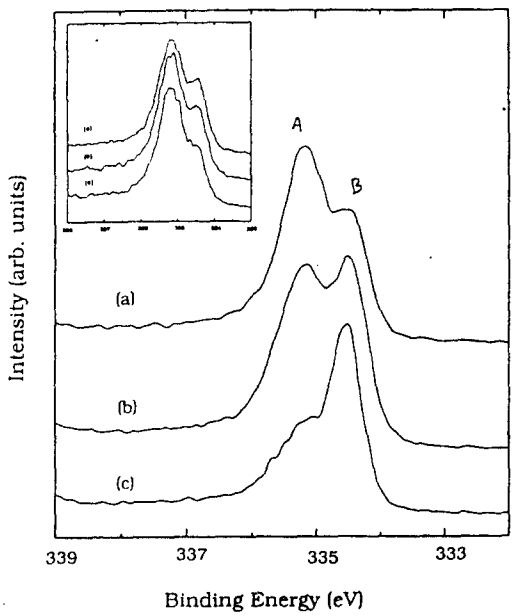


Fig 2. The Pd $3d_{5/2}$ with composition

The angles are (a) $0^0$, (b) $30^0$ and (c) $70^0$ from the surface normal. Up to this point, two things are apparent. First, in case of Pd, there are two different chemical environments. One(peak A) has more surface related than another. ,Second, the intensity of peak B which is less sensitive to surface, is proportional to the concentration of Ag. So there is no doubt that this is more less related to the alloy phase. In summary, we have shown the surface induced phase separation in Pd-Ag alloy system at room temperature. These separated phases can be mixed after the sample heated up to $600^0$C. This is reversible process but the time constant for the same separation is relatively large. One can enhance this phase separation by ion irradiation.