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ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY OF Pd-Si GLASSES

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In order to determine systematic changes in the density of states with alloy composition, photoelectron spectra at $h\nu=21.2$ eV were measured for several amorphous alloys based on the well-known Pd-Si glass system. Three binary alloys with 15, 20, and 25 at. % Si, two ternaries, Pd₈₀Si₁₇Cu₃ and Pd₈₀Si₁₄Cu₆, and polycrystalline Pd were analyzed. Compared to Pd, both the density of states at the Fermi energy and the d-band width are reduced in the glasses. The d-bands display an overall shift of 0.4 eV over the range of alloy compositions studied. Partial agreement with recent density of states calculations was obtained.

In this communication we present photoelectron spectra for several different compositions of Pd-Si metallic glass alloys. Previously published results¹ for Pd_{77.5}Si_{16.5}Cu₆, have indicated the need for measurements of the compositional dependences of the electronic density of states in these systems. Photoelectron spectra at $h\nu=21.2$ eV were obtained for three binary alloys, with 15, 20, and 25 at. % Si, two ternaries, Pd₈₀Si₁₇Cu₃ and Pd₈₀Si₁₄Cu₆, and polycrystalline Pd.

The ultrahigh vacuum, photoemission apparatus employed in this investigation was described earlier.² The amorphous samples, approximately 8mm x 10mm x .04mm, were cut from thin ribbon stock. The sample holder accommodated three samples so that a group of different compositions could be loaded prior to system bakeout. This served to facilitate the comparisons among the different compositions by exposing them to the same treatment during preparation. Also, one sample of a composition studied earlier was included in a subsequent group to ensure reproducibility of the spectra for each alloy. To preclude sample recrystallization, the system bakeout was limited to <140°C for ~24 hours. After this low-temperature bakeout the base pressure was ~10⁻⁸ Pa (1 x 10⁻¹⁰ Torr), or less. Each sample was cleaned prior to measurement by sputtering with a beam of 500 eV argon ions.⁴ A photoelectron spectrum was started ~1-1/2 minutes after the end of bombardment and required ~4 minutes for completion. Data were collected for a photon energy of 21.2 eV, with an electron energy analyzer resolution of ~.25 eV.

The spectra for Pd and the five amorphous alloys are presented in Fig. 1. The alloy spectra were amplified slightly (vertically) for normalization to the main Pd peak near -2 eV. Only the upper 7 eV range is shown because (at least for $h\nu=21.2$ eV) the electron distributions below ~-5 eV are featureless,

displaying no structure. It should be mentioned, however, that contamination was found to produce small peaks of ~1 eV halfwidth appearing at ~-6 and -8.5 eV after ~20 minute of exposure to the 10⁻¹⁰ Torr ambient vacuum (mainly H₂ and CO). The width of the Pd d-band (dashed curve a) for $h\nu=21.2$ eV is considerably narrower than calculations.⁵ This probably results from a matrix element effect for the lowest part of the Pd d-band near ~-4 eV, which is strongly s-hybridized.⁶ For $h\nu=40.8$ eV,^{7,18} this portion of the d-band was seen to grow in prominence. Curve b (Pd₇₅Si₂₅), representative of the remaining glassy alloys, overlays the Pd spectrum for comparison. Nagel, et al¹ showed that for Pd_{77.5}Si_{16.5}Cu₆, the density of states near the Fermi energy was reduced relative to Pd. Similar behavior for three binary Pd-Si alloys¹⁴ was obtained recently. Our data show that this condition prevails for all the alloys studied, with the result that no obvious stability criteria in terms of the density of states at the Fermi level could be determined.

The shapes of the spectra for the glassy alloys (curves b-f) are (within noise) identical across the band from ~-5 to -1 eV; the only differences occurring in the ~1 eV range near E_F, where the main band blends into the shoulder near the Fermi edge. The whole band, however, shifts with alloy composition. The positions of the main peaks (i.e., binding energies referenced to E_F) for the data of Fig. 1 are plotted in Fig. 2 against silicon content. The peak position with respect to the Fermi energy was taken as the centerline of the upper, ~7% of the peak, which was the only symmetric portion of each peak.⁸ The binding energies for the binaries (open circles) essentially show a linear dependence on silicon content, varying by almost 0.4 eV for a change in silicon from 15 to 25%. In contrast, the ternaries (crosses) fall outside the straight-

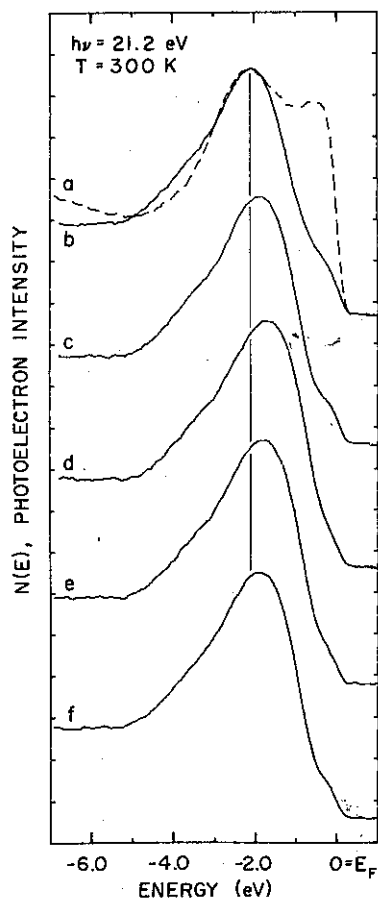


Fig. 1 Normalized photoelectron spectra for $h\nu=21.2$ eV. (a) (dashed) - polycrystalline Pd; (b) through (d) - binary amorphous alloys, $\text{Pd}_{75}\text{Si}_{25}$, $\text{Pd}_{80}\text{Si}_{20}$, $\text{Pd}_{85}\text{Si}_{15}$, resp.; (e) and (f) - ternaries, $\text{Pd}_{80}\text{Si}_{17}\text{Cu}_3$, $\text{Pd}_{80}\text{Si}_{14}\text{Cu}_6$, resp. The vertical line drawn at the position of the $\text{Pd}_{75}\text{Si}_{25}$ peak is meant to serve as a reference to show peak shifts.

line, binary fit. In fact, if we consider the ternaries in terms of increasing copper content, and include the binary $\text{Pd}_{80}\text{Si}_{20}\text{Cu}_0$, we can see from Fig. 2 that a minimum is indicated at $\sim 17\%$ Si, for the binding energy (with respect to E_F) of the d-band peak. Thus, although copper contributes no obvious structure to the spectra of the ternaries, it does appear to inhibit the upwards shift of the d-band peak as the silicon content is reduced. Interestingly enough, this minimum is in the compositional range of $\text{Pd}_{77.5}\text{Si}_{16.5}\text{Cu}_6$, which is a very easy glass former, and therefore is suggestive of a stability criterion for the glasses. Obviously, however, to definitely establish this connection, a study covering a more comprehensive range of alloy compositions near the minimum is called for.

As was mentioned earlier, the bands for

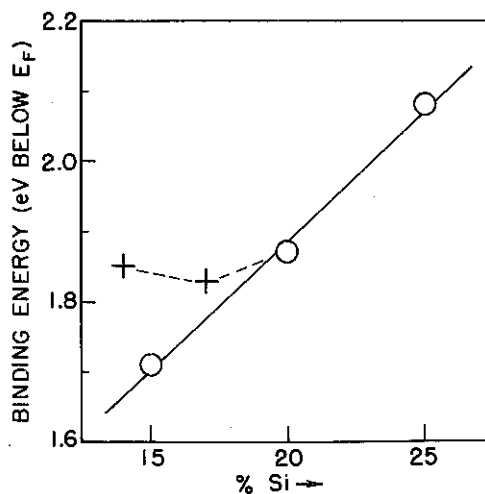


Fig. 2 d-band peak with respect to E_F position versus silicon content for the data of Fig. 1. Open circles - binaries; crosses - ternaries. The solid line is a straight line fit to the binaries. The dashed line connects the ternaries. Relative binding energies are estimated to be in error by no more than ± 30 meV.

the different alloys are essentially identical, differing only in the region of the shoulder near E_F . Also, there seem to be no relative changes in strength across the spectrum as the ratio of Si to Pd changes. The shift in energy with composition of the binaries is reminiscent of a rigid band shift to higher binding energies as charge is transferred to the Pd band from increasing amounts of Si. Riley, et al.⁹ recently studied glassy $\text{Pd}_{81}\text{Si}_{19}$ and concluded that the relaxation energy for Pd core levels is 0.3 eV smaller than for Pd metal. They argue approximately from this that charge transfer is negligible. Our compositional studies indicate that a further shift of ~ 0.4 eV remains to be accounted for and we believe that this cannot be ascribed to changes in the relaxation energy. Wertheim, et al.¹⁰ showed that significant charge is transferred to Cu, Ag, and Au in alloys with Zn, Cd, and Mg. The present data are similar to theirs in that the compositional shifts are in the position of d-bands below the Fermi level, and we can parallel their argument¹⁰ that the relaxation energy shifts are small. Therefore, we are inclined to assume that the spectra result from mainly probing the Pd d-electron contribution to the band structure, and that the Si contribution is relatively suppressed at $h\nu=21.2$ eV by a matrix element effect for the Si-p electrons. In Fig. 1, curves a and b, the overlap region near -4 eV shows that the skewing towards lower energy of the glassy alloy spectra arises from an increase in strength relative to the main d-band peak at ~ -2 eV. The enhancement of this region of the glasses relative to crystalline Pd may be the result of a change in character of this region from

strongly s-d, in crystalline Pd, to p-d in the glass.

Kelly and Bullett¹¹ recently calculated the density of states for amorphous Pd₄Si, based on the structural models of Boudreaux.¹² Their preliminary results are in reasonable agreement with our spectra with regards to shape, however, some adjustments are indicated

for a more favorable energy fit, in particular, the overall width of the calculated bands is about twice the measured values. Kelly¹³ has recently completed calculations for Pd₇₅Si₂₅ and Pd₈₅Si₁₅. The shapes and widths of the calculated bands do not vary with composition but the peak shifts toward the Fermi energy with metalloid addition, contrary to observation.

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3. Samples were prepared by a melt spinning process using quartz crucibles. The alloys were prepared from 99.997% pure components which resulted in compositions within 0.1% of nominal. All samples were x-rayed to assure non-crystallinity.
4. Typically 5 minutes at 5 μ A for an argon pressure of 5x10⁻⁵ Torr. The effect of ion bombardment on the alloy composition at the surface could not be determined in the present apparatus. However, in another study (Ref. 14) of similar Pd-Si alloys, inelastic ion-scattering spectroscopy (ISS) showed no drastic deviation from the bulk composition.
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