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ELECTRONIC STRUCTURE OF $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ METALLIC GLASS

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Abstract. In-house photoemission and inverse-photoemission spectra (PES and IPES) were measured on $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $Pd_{40}Ni_{40}P_{20}$ bulk metallic glasses together with incident photon-energy dependent PES spectra using synchrotron radiation. Minima are observed at slightly higher energy than the Fermi level. Pd 4*d*, Ni 3*d* and Cu 3*d* partial density of states were estimated from the PES and soft X-ray emission spectra, and the feature of the electronic structure in these glasses were discussed in detail in connection to the excellent glass-forming ability.

1. INTRODUCTION

Bulk metallic glasses of Pd-Ni-Cu-P alloys, discovered by Nishiyama and Inoue [1], have intensively been investigated due to their good glass-forming abilities (GFA). They have optimized the concentration dependence of the critical-cooling-rate, and found that $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ has at present the slowest critical-cooling-rate of 0.067 K/s and can form a massive bulk glass with a diameter of more than 40 mm by simple water-quenching [2]. Several attempts have been made from the viewpoints of its structural and electronic properties to understand why it has such an excellent GFA.

We have recently investigated electronic density of states (DOS) of the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ glass by photoemission spectroscopy (PES) using synchrotron radiation [3]. For the further study of the electronic DOS, we have measured inverse-photoemission spectra (IPES) to obtain the conduction-band DOS. In addition, PES and IPES experiments were carried out on the reference glass $Pd_{40}Ni_{40}P_{20}$, which has a slightly worse critical-cooling-rate of 1.6 K/s [4]. In this paper, we present the PES and IPES results of these glasses, and discuss the feature of the electronic structure in these bulk metallic glasses.

2. EXPERIMENTAL PROCEDURE

The samples were prepared as follows. Prior to making the master ingots, a Pd-P pre-alloy was prepared using a high-purity P polycrystal. Then, the master ingots were made by arc-melting the mixtures of pure Pd, Ni, Cu, and the pre-alloyed Pd-P in Ar atmosphere. The purities of Pd, Ni, Cu, and P were 99.95, 99.9, 99.99, and 99.9999%, respectively. In order to eliminate heterogeneous nuclei due to oxide contamination, a B_2O_3 flux treatment [5] was repeatedly (typically ten times) carried out in highly purified Ar atmosphere (less than ten ppm oxygen content) during the alloy prepara-

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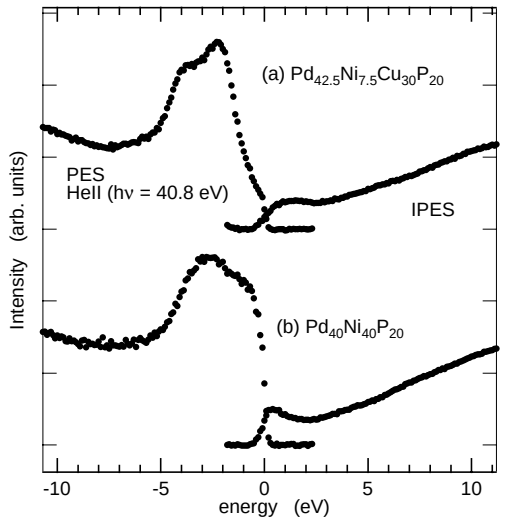

Fig. 1. The valence- and conduction-band DOS of the (a) $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and (b) $Pd_{40}Ni_{40}P_{20}$ glasses obtained from in-house PES and IPES measurements, respectively.

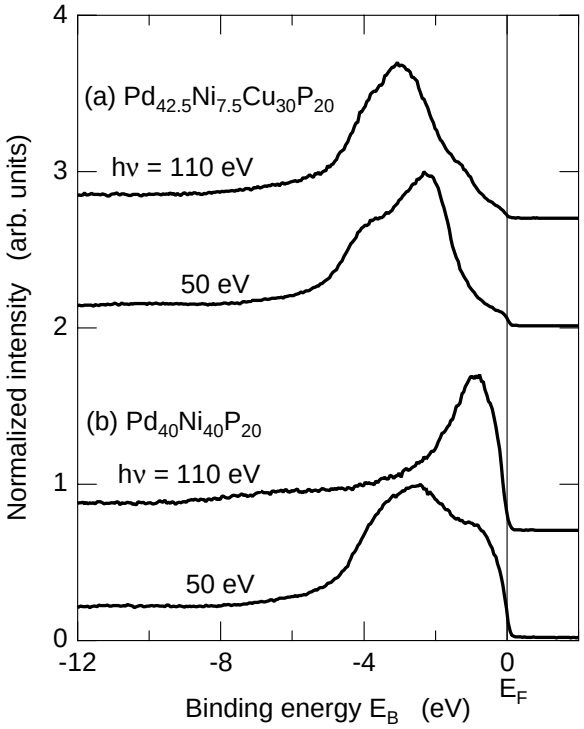

Fig. 2. The PES spectra at $h\nu$ = 50 and 110 eV of (a) $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and (b) $Pd_{40}Ni_{40}P_{20}$ glasses as a function of the binding energy, E_B.

tion. The melts in quartz ampoules with an inner diameter of 3 mm were kept at about 1273K for at least six days, and then quenched in water. The absence of crystallinity in the samples was confirmed by X-ray diffraction and calorimetry. The composition of the samples was examined to be within 1% by an electron-probe micro-analysis method before and after the experiments.

The in-house PES and IPES spectra were obtained using the ultraviolet PES and IPES spectrometers mounted in ultrahigh vacuum chambers with the base pressures of $1 \cdot 10^{-9}$ and $1 \cdot 10^{-10}$ mbar, respectively. The PES spectrometer is composed of an He discharge lamp with the incident photon energy, $h\nu$, of 40.8 eV and a double-stage cylindrical-mirror analyzer (DCMA). Pass energy of photoelectrons was fixed to be 16.0 eV with the corresponding energy resolution of 0.2 eV. The IPES spectrometer [6] is made up of a low-energy electron gun of Erdmann-Zipf type with a BaO cathod and a band-pass-type photon detector centered at 9.43 eV. The IPES spectra were measured with the bremsstrahlung isochromat mode with a total energy resolution of 0.56 eV.

The incident-energy dependent PES experiments were carried out at the beamline BL7 of Hiroshima Synchrotron Radiation Center. Ultraviolet photons from the storage ring HiSOR were monochromatized with a Dragon-type monochromator, and the PES data were taken with a hemispherical photoelectron energy-analyzer (GAMMA-DATA SCIENTA SES100). The total energy resolution of the PES spectrometer was about 0.2 eV at $h\nu$ = 100 eV. The details of the experiment are given elsewhere [3].

All the spectra were collected at room temperature. Clean surfaces were *in situ* obtained by scraping the samples with a diamond filer in a sample preparation chamber attached with the analyzer ones, which were kept under ultrahigh vacuum below $1 \cdot 10^{-10}$ mbar. Any changes of the spectral features due to oxygen or carbon contamination were not visible within 24 h after the sample cleaning, and the measurements were performed within 12 h. The energy of all spectra was defined with respect to the Fermi energy, E_F, determined from the spectra of a freshly evaporated Au film.

3. RESULTS

Fig. 1 shows the valence- and conduction-band DOS of the (a) $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and (b) $Pd_{40}Ni_{40}P_{20}$

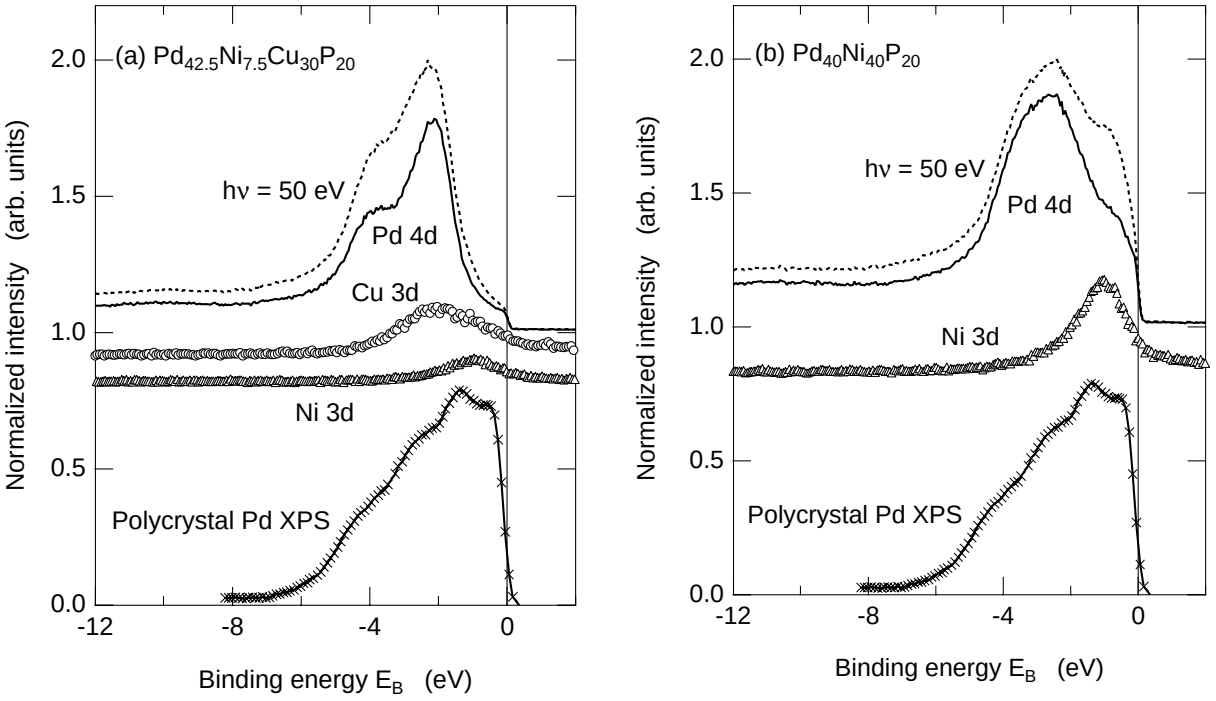

Fig. 3. The Pd 4*d* partial DOS (solid curves) calculated from the *h*ν dependent PES spectra of (a) $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and (b) $Pd_{40}Ni_{40}P_{20}$ glasses. The PES spectrum of the polycrystal Pd (crosses) measured by XPS using Mg K_α radiation (*h*ν = 1254 eV) and the Ni (triangles) and Cu 3*d* (circles) partial DOS obtained by SXES are also given.

glasses obtained from in-house PES and IPES measurements, respectively. The PES and IPES spectra are connected so that the $N(E_F)$ values coincide with each other. The PES spectra of both the glasses are in good agreement with our synchrotron radiation results at 40 eV [3], which will be given later. The intensities of PES spectra are much larger than the IPES spectra, and these peaks and shoulders would originate from the Pd 4*d*, Ni 3*d*, and Cu 3*d* localized states [3]. It should be noted that the magnitudes of $N(E_F)$ are small in general, and even more suppressed by replacing Ni atoms with Cu atoms. In each conduction-band DOS, a minimum is seen at a slightly higher energy than E_F, although the background of the spectrum is not estimated for the subtraction.

Fig. 2 shows the PES spectra at *h*ν = 50 and 110 eV of (a) $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ [3] and (b) $Pd_{40}Ni_{40}P_{20}$ glasses as a function of the binding energy, E_B. The spectra are normalized to the maximum intensities, and the intensity of the actual spectra rapidly decreases with increasing *h*ν, which is due to rapid decreases of the photoionization crosssections, σ_p, of the elements with increasing *h*ν.

4. DISCUSSION

The electron configurations of Pd, Ni, Cu, and P are respectively $4d^{10}$, $3d^8 4s^2$, $3d^{10}4s^1$, and $3p^3$. Thus the vicinity of E_F is mainly composed of highly localized Pd 4*d*, Ni 3*d*, and Cu 3*d* electrons, and probably extended 3*p* electrons with small portions of extended Ni 4*s* and Cu 4*s* electrons. In order to understand the composition of the obtained DOS, the *h*ν dependence of the PES spectra is very helpful. For this the knowledge of the *h*ν dependence of σ_p is important, which was calculated by Yeh and Lindau [7] as Fig. 2 of Ref. [3]. With increasing *h*ν from 50 to 110 eV, the σ_p of Pd 4*d* electrons very rapidly decreases from about $20 \cdot 10^{-24}$ cm^2 to almost zero, while those of Ni and Cu 3*d* electrons slightly decrease, and that of P 3*p* electrons is very small all over the energy range above. Therefore, it is reasonable to mention that the PES spectrum of these glasses at *h*ν = 110 eV is composed of

mainly Ni and/or Cu 3*d* electrons, while the Pd 4*d* electrons dominate (by about 70%) the PES spectrum at $h\nu$ = 50 eV in addition to the Ni and/or Cu 3*d* contributions.

From the $h\nu$ dependence of the PES spectra, thus, one can estimate the Pd 4*d* partial DOS, which is shown as solid curves in Fig. 3. The PES spectrum of the polycrystal Pd [8] measured by X-ray photoemission spectroscopy (XPS) using Mg K_α radiation ($h\nu$ = 1254 eV) is also given at the bottom of the figure as a reference. Of particular interest is that the Pd 4*d* partial DOS in both the glasses are very different from the Pd XPS result. Firstly, the DOS at E_F is highly suppressed compared to the XPS data. Secondly, the peaks at the two highest energies of –0.5 and –1.4 eV in the Pd polycrystal XPS result are (a) completely missing or (b) highly suppressed in the Pd 4*d* partial DOS. Since the Pd 4*d* states are highly localized in general, these differences cannot be explained by the difference of phases. On the other hand, the partial Ni and Cu 3*d* DOS obtained by soft X-ray emission spectroscopy (SXES) [9] shown at the bottom of the figures, indicate features similar to those of XPS data of the pure polycrystals given in Figs. 3 and 4 in Ref. [3]. Therefore, the present results of the $h\nu$ dependence of the PES spectra strongly inspire a formation of a new correlation around the Pd atoms in these metallic glasses. Although the P 3*p* partial DOS cannot be estimated by the present PES experiment due to the small σ_p value, we can intuitively suppose that covalent bonds may be newly formed between Pd and P atoms selectively, which has for a long time been discussed as a typical short-range order around the P atoms [10].

Detailed observations of the present PES results indicate that compare to the reference $Pd_{40}Ni_{40}P_{20}$ glass, the $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ glass has the better GFA and the smaller $N(E_F)$ value. This result seems to support the Nagel-Tauc [11] prediction that the good GFA is closely related to the decrease of $N(E_F)$ within the framework of nearly-free-electron model. However, the $Pd_{40}Cu_{40}P_{20}$ glass has the worse GFA and the smaller $N(E_F)$ value [8] than those in $Pd_{40}Ni_{40}P_{20}$ glass, which contradicts the prediction. Our partial analysis of the DOS in Fig. 3 showed that Ni 3*d* localized electrons dominates $N(E_F)$, and the magnitudes of minima appeared at slightly higher energy than E_F shown in Fig. 1 look similar to each other. In addition, the Nagel-Tauc prediction is based on the extended electronic states. Therefore, the propriety of the Nagel-Tauc prediction cannot be proved by the present DOS studies, and a detailed investigation on the extended *sp* partial DOS would be necessary. The present DOS result is more likely a consequence of a bonding and antibonding splitting participating in Pd-P bonds with an enhanced covalency in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ bulk metallic glass compared to the reference $Pd_{40}Ni_{40}P_{20}$ glass.

5. CONCLUSION

In-house PES and IPES spectra were measured on $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $Pd_{40}Ni_{40}P_{20}$ bulk metallic glasses together with $h\nu$ dependent PES spectra using synchrotron radiation. Minima are observed at slightly higher energy than the Fermi level. The Pd 4*d*, Ni 3*d* and Cu 3*d* partial DOS were estimated from the PES and SXES, and the feature of the electronic structure in these glasses were discussed in detail in connection to the excellent GFA.

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