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Electronic structures and heterogeneity of Zr-Cu-Ag metallic glasses

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ABSTRACT

Photoemission and inverse-photoemission spectroscopy (PES and IPES) measurements were carried out on $Zr_{50}Cu_{50}$, $Zr_{45}Cu_{45}Ag_{10}$, and $Zr_{40}Cu_{40}Ag_{20}$ metallic glasses to investigate the valence- and conduction-band electronic structures, respectively. From the incident photon energy, $h\nu$, dependence of the PES spectra, partial DOSs of *s* and *d* electrons for the constituent elements were estimated, and it was found that the DOS near E_F is mainly composed of Zr 4*d* electrons and the Cu 3*d* electrons are localized in the valence band. Core-level PES measurements were also performed at the Zr 3*d*, Cu 3*p*, and Ag 3*d* levels. The Zr 3*d* core spectra indicate three chemical states in all of these glasses, suggesting a chemical heterogeneity. Energy shifts are observed in the Zr 3*d* core levels, indicating the charge transfer in the Zr-Cu-Ag metallic glass system.

1. Introduction

In the recent two decades, bulk metallic glasses (BMGs) with distinct glass transitions have been discovered in various multi-component metallic alloys. They show extremely excellent glass-forming abilities (GFAs), where even a very slow cooling rate such as 1 Ks^{-1} can avoid crystallization. Physical and technological properties of these BMGs were well investigated, including glass transitions, structural changes, phase stabilities, elastic constants, magnetic properties, etc. [1]. Among these BMGs, the Zr-Cu alloys strongly improve the GFAs by adding Al, having a critical cooling rate of some Ks^{-1} and allowing to form a massive BMG with a diameter of about 10 mm [2].

Zhang et al. [3] reported that by adding Ag to $Zr_{50}Cu_{50}$ alloy, the GFA greatly improves as Al, and the critical sample diameter (d_c) manufactured with a Cu mold tilt casting increases with increasing Ag content up to $d_c = 6$ mm at 10 at. % Ag. The further addition of Ag, however, degrades the GFA, e.g., $d_c = 2$ mm at 16 at.% Ag [3].

Louzguine-Luzgin et al. [4] measured high-energy X-ray diffraction on $Zr_{45}Cu_{55}$, $Zr_{45}Cu_{45}Ag_{10}$, and $Zr_{45}Cu_{35}Ag_{20}$ glassy alloys to examine the total structural effect of the Ag addition on these alloys, and it was suggested that the addition of Ag causes a formation of a more *homogeneous* local atomic structure compared with that of the binary Zr-Cu alloy, which could be considered as a reason for the improved GFA in this alloy. On the other hand, Fujita et al. [5] concluded from an *ab initio* molecular dynamics (MD) simulations and Zr, Cu, and Ag *K* x-ray absorption fine structure (XAFS) measurements that an atomic-scale *heterogeneity* may play an important role in improving the GFA.

Kawamata et al. [6] performed anomalous X-ray scattering (AXS) in combination with reverse Monte Carlo (RMC) modeling to investigate intermediate-range local structure experimentally, and concluded that the improvement in the GFA appears to be associated with the local coordinations around the Ag and Cu atoms. Hosokawa et al. [7] also carried out AXS combined with the complementary neutron diffraction (ND). The analysis using RMC revealed that only the Zr-Ag partial structure factor indicates an intermediate-range atomic correlation, and the Cu and Ag slightly exhibit the phase separation tendencies.

Although the above structural studies gave information about the structure-property relationship in the Zr-Cu-Ag BMG, critical structural reason on the GFA was not yet clarified, or even the existence of the structural *heterogeneity* is still controversial as mentioned above. Thus, a different view is necessary to clarify the structure of BMGs. We have measured electronic structures on several Pd-based BMGs, such as $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ [8,9], $Pd_{40}Ni_{40}P_{20}$ [8,9], $Pd_{40}Cu_{40}P_{20}$ [9], and $Pd_{30}Pt_{17.5}Cu_{32.5}P_{20}$ [10], by measuring photoemission and inverse photoemission spectroscopies (PES and IPES). We found that the Pd 4*d* electrons in the valence band are highly localized, compared with those in pure Pd metal. It was also concluded that the P 2*p* core levels in these Pd-based BMGs clearly separate into two states, indicating that the P atoms have two different chemical sites, which is a strong proof for the existence of an elastic *inhomogeneity* [9,10]. Furthermore, the Pd $3d_{5/2}$ core level in $Pd_{30}Pt_{17.5}Cu_{32.5}P_{20}$ exhibits a band broader than those in $Pd_{42.5}Ni_{7.5}Cu_{30}P_{20}$ and $Pd_{40}NiCu_{40}P_{20}$, suggesting that the local

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structures around the Pd atoms become *heterogeneous* by replacing Ni with Pt [10].

As shown in our previous works, electronic structures in BMGs are highly feasible to investigate local environments with element-selective. Recently, we have performed valence-band and core-level PES and conduction-band IPES measurements on $Zr_{45}Cu_{45}Ag_{10}$, $Zr_{40}Cu_{40}Ag_{20}$, and the reference $Zr_{50}Cu_{50}$ metallic glasses with d_c = 6, 2 [3], and 2 mm [11], respectively, to investigate local structures from the viewpoint of electronic structures. In this paper, we report results of the PES and IPES measurements, and discuss the features of element-selective *heterogeneity* in these metallic glasses in detail.

2. Experimental procedure

The Zr-Cu-Ag alloy ingots with nominal compositions were prepared by arc-melting the mixtures of Zr, Cu, and Ag metals with purities of 99.5, 99.99, and 99.99%, respectively, in a high-purity Ar atmosphere. For the $Zr_{45}Cu_{45}Ag_{10}$ alloy, a cylindrical rod of ~3 mm in diameter and ~10 mm in length was manufactured by a tilt casting method with a Cu mold. The $Zr_{40}Cu_{40}Ag_{20}$ and the reference $Zr_{50}Cu_{50}$ amorphous ribbons of ~0.03 mm thick and ~2 mm width were prepared by a single roller-spinning technique in Ar atmosphere.

The PES spectra were measured using a spectrometer installed at the beamline BL-7 of Hiroshima Synchrotron Radiation Center (HSRC), Hiroshima University, Higashi-Hiroshima, Japan. The schematic view of the PES spectrometer is exhibited in Fig. 1(a). Ultraviolet photons generated from a compact electron-storage ring (HiSOR) with the ring energy of 700 MeV and the ring current of 160–300 mA were monochromatized with a Dragon-type monochromator, covering the incident photon energy, $h\nu$, values from 20 to 450 eV. A PES spectrometer with a hemispherical photoelectron energy-analyzer (GAMMA-DATA, SCIENTA SES2002) attached to the analyzer chamber under the ultrahigh vacuum below 1×10^{-8} Pa at the end-station of BL-7, was used for the PES experiments. The overall energy resolution, ΔE, of the spectrometer was about 0.1–0.5 eV depending on the $h\nu$ values of 20–450 eV. The details of the PES experimental setup are given elsewhere [12].

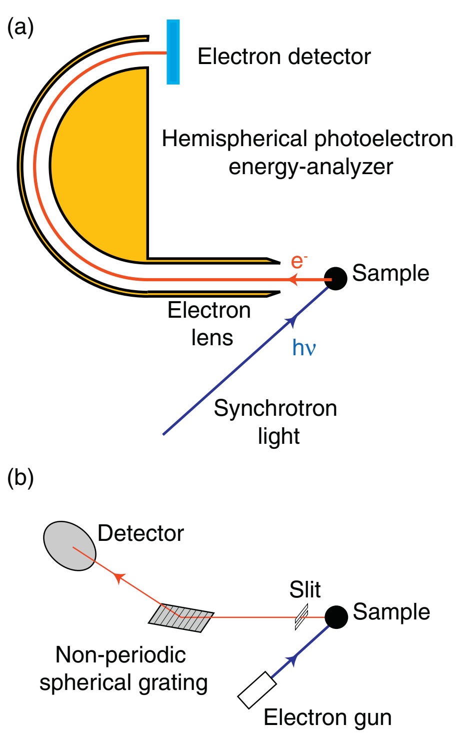

Fig. 1. Schematic views of the (a) PES and (b) IPES spectrometers used for the present work. The figures are taken from Ref. [13].

All the PES spectra were collected at room temperature. Clean surfaces were *in situ* obtained by sputtering the samples with Ar^{+} ions in a sample preparation chamber with the base pressure below 1×10^{-8} Pa. No core spectra due to surface contaminations were visible within 24 h after the sample surface cleaning, and the measurements were performed within 12 h. The energies of all spectra were defined with respect to the Fermi energy, E_F, of the sample or a freshly evaporated Au film.

The IPES experiments were carried out at the resonant inverse-photoemission spectroscopy (RIPES) station in the HSRC. The schematic view of the IPES spectrometer is exhibited in Fig. 1(b). The self-developed IPES spectrometer is equipped with a low-energy electron gun, a non-periodic spherical grating and a one-dimensional photon detector. The total energy resolution was ~0.5 eV at the electron gun energy E_k of 50 eV. The energy of the IPES spectra is referred to E_F, determined from the Fermi edge of the IPES spectra of a Au film.

All the IPES experiments were also carried out 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 one, both of which were kept under ultrahigh vacuum below 1×10^{-8} Pa.

3. Results

Fig. 2 shows the structure factors $S(Q)$ of $Zr_{50}Cu_{50}$, $Zr_{45}Cu_{45}Ag_{10}$, and $Zr_{40}Cu_{40}Ag_{20}$ metallic glasses measured by neutron diffraction (ND), the first two of which were already published in Figs. 1(a) and 2(a) of Ref. [7]. The samples are the same as those used for the present PES and IPES measurements to examine the glass phase of the samples. The ND experiment was carried out using the High Intensity Total Diffractometer (NOVA) installed at the beamline BL21 of Materials and Life Science Experimental Facility (MLF) in Japan Proton Accelerator Research Complex (J-PARC), Tokai, Japan. As clearly seen in the figure, no crystalline peaks are observed. With increasing the Ag concentration in the glasses, both of the second and third peaks at about 47 and 73 nm^{-1}, respectively, become larger. However, there seems to be no relation the GFA of the samples because the increases are monotonous with the Ag concentration.

Fig. 3(a) shows the valence-band PES and conduction-band IPES spectra of the reference $Zr_{50}Cu_{50}$ metallic glass with d_c = 2 mm indicated as the solid and dashed curves, respectively. The spectra are normalized to the corresponding maximum intensities. The $h\nu$ value for the PES measurements varies from 39 to 150 eV as indicated upper-left of each spectrum. The PES spectra are displaced by 0.5 for clarity. The intensity of the actual PES spectra decreases with increasing $h\nu$ due to

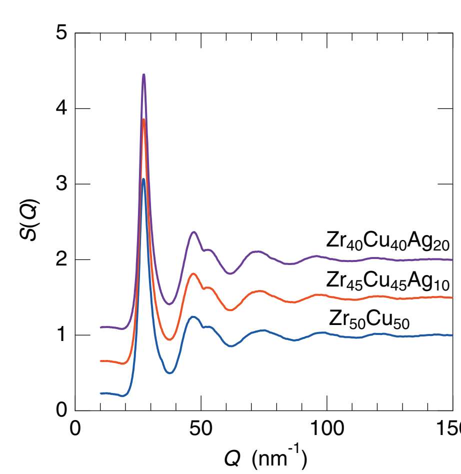

Fig. 2. The $S(Q)$s of $Zr_{50}Cu_{50}$, $Zr_{45}Cu_{45}Ag_{10}$, and $Zr_{40}Cu_{40}Ag_{20}$ metallic glasses measured by ND. The $S(Q)$ data are displaced by 0.5 for clarity.