



The electronic properties of nickel phosphide surfaces: Angle-resolved and resonant photoemission studies

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ABSTRACT

The electronic structures of (1×1) Ni₂P(0001) and $c(2 \times 4)$ Ni₂P(10 $\bar{1}$ 0) have been investigated by photoemission spectroscopy (PES). For both surfaces, the valence PES spectra consisted of a Ni 3d–P 3p hybrid band (main band) and a satellite; the main band is observed at 0–4 eV and the satellite is observed at 8 eV. Resonant PES study showed that the satellite is associated with the photoemission process leading to a two-hole bound final state. On (10 $\bar{1}$ 0), a P 3p-induced surface state is formed around 0.6 eV along the boundary of the surface Brillouin zone of the $c(2 \times 4)$ lattice. The surface core-level shifts were observed in P 2p spectra for both surfaces; the surface components were shifted to the lower binding energy side by 0.9 eV for (0001) and by 0.6 eV for (10 $\bar{1}$ 0). These results suggest that the coordination number of surface P atoms is much reduced from that in the bulk. The segregation behavior of P atoms in Ni₂P was investigated by Auger electron spectroscopy and PES. It was found that the segregation of P atoms proceeds by annealing at 260–330 °C. The valence PES study showed that the 3d levels of the surface Ni atoms are stabilized through the bonding with segregated P atoms.

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1. Introduction

The surface properties of transition metal phosphides (TMPs) have attracted much attention because these materials have recently been shown to form an interesting new group of catalysts active for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) for petroleum fuels [1]. It has become important to search new catalysts for these reactions with the activity higher than currently used sulfide-based catalysts, because the allowed S content in fuels is becoming lower while S content in crude oil is becoming higher. TMP is one of the promising candidates as catalyst for HDS and HDN in the next generation. Of all TMPs studied thus far, Ni₂P has been found to have the highest catalytic performance for these reactions [1]. In order to obtain the microscopic understanding as to the origin of the high catalytic performance, it is necessary to elucidate the properties of Ni₂P single-crystal surfaces. The Ni₂P crystal has a hexagonal Fe₂P-type structure, and the crystal consists of two types of atomic layers with the stoichiometry of Ni₃P and Ni₃P₂ which are stacking alternatively along the [0001] direction. The characterization of Ni₂P single-crystal surface has been mainly attempted for a (0001) surface. An ideal (0001) surface should be terminated with either a Ni₃P- or a Ni₃P₂-layer, and theoretical studies using DFT calculations have predicted that a

Ni₃P₂-terminated surface is more stable [2,3]. However, previous structural analyses have revealed that, in addition to a (1×1) termination, the surface shows several reconstructed phases such as $3/2 \times 3/2$ and $\sqrt{3} \times \sqrt{3} R30^\circ$ [4–8]. Furthermore, Hernandez et al. proposed from dynamical low-energy electron diffraction (LEED) analyses that the (1×1) surface is not an ideal surface and should be a Ni₃P₂-terminated surface on which P atoms sit above three-fold sites of three Ni atoms (P-terminated Ni₃P₂-surface) [8]. As for the electronic structure, our group performed photoemission spectroscopy (PES) study on Ni₂P(0001) and found that the spectra consist of a Ni 3d–P 3p hybrid band (main band) and a satellite; the main band is observed at 0–4 eV and the satellite is observed at 8 eV [9,10]. In contrast to the case for (0001), relatively few studies have been performed on the other Ni₂P low-index surfaces. Recently Guo et al. studied the structure of Ni₂P(10 $\bar{1}$ 0) by LEED and scanning tunneling microscopy (STM), and proposed that the surface is reconstructed to give a $c(2 \times 4)$ periodicity [11]. The recent PES study revealed that the spectral features of the main band and the satellite of (10 $\bar{1}$ 0) were similar to those of (0001). However, it has been also revealed that there are some surface states on (10 $\bar{1}$ 0) [12]. The aim of this study is to elucidate the electronic structures of these surfaces by angle-resolved PES (ARPES) utilizing synchrotron radiation. The consistency between the ARPES data and the previously published structural models will be discussed.

Recent studies of the structures of (1×1) Ni₂P(0001) [8] and $c(2 \times 4)$ Ni₂P(10 $\bar{1}$ 0) [11] have suggested that both of the topmost layers of these surfaces are composed of P atoms, which should

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be segregated from the bulk. Major roles of the P atoms in HDS are expressed as “ligand effect” and “ensemble effect”, which mean the stabilization of the 3d levels of Ni atoms due to the bonding with P atoms and partial block of the active Ni sites by P atoms, respectively [2]. These effects are expected to make the surface activity moderate and to prevent the deactivation of the surface induced by accumulation of S adsorbates on active Ni sites, and thus surface P atoms should play crucial roles on the preservation of catalytic activities of TMPs. These effects should be enhanced by the segregation of P atoms, and thus the surface activity for HDS is closely related with the segregation behavior of P atoms. In this paper, segregation behavior of P atoms induced by heat treatment and its effects on the surface electronic structure of $\text{Ni}_2\text{P}(10\bar{1}0)$ are investigated by Auger electron spectroscopy (AES) and PES.

2. Experimental

The ARPES measurements were performed at the beam lines (BL) 1C and 3B of the Photon Factory, High Energy Accelerator Research Organization (KEK). Photoelectrons were collected by an electron energy analyzer of 180° -sector hemispherical type (VSW HA54) with an acceptance angle of $\pm 1^\circ$. The total experimental resolution was estimated from the Fermi edge in the spectra of a Ta sample holder, and was estimated to be 120 meV at $h\nu = 40$ eV at BL-1C and 250 meV at $h\nu = 74$ eV at BL-3B. The spectra presented below were normalized by the photocurrent of the gold mesh which was inserted at the entrance of the analysis chamber for those obtained in BL-1C and by the photocurrent of the final stage mirror for those obtained in BL-3B. The incidence angle of the light (θ_i) and detection angle of photoelectrons (θ_d) are given relative to the surface normal. The base pressure in the vacuum system was 1×10^{-10} Torr.

The Ni_2P single-crystal was grown by Dr. Otani of National Institute for Materials Science. The crystal was cut at orientations of (0001) and $(10\bar{1}0)$ by spark erosion into disks of 1 mm thickness, and the surfaces were subsequently polished mechanically to a mirror finish. The surfaces were cleaned in a vacuum chamber by Ar^+ ion sputtering (3 keV, 20 μA , 30 min) and annealing at 600°C for (0001) and 400°C for $(10\bar{1}0)$. The (0001) and $(10\bar{1}0)$ clean surfaces prepared by these procedures gave sharp (1×1) and $c(2 \times 4)$ LEED patterns, respectively.

3. Results and discussion

3.1. Surface electronic structures

Fig. 1 shows ARPES spectra of $\text{Ni}_2\text{P}(0001)$ and $(10\bar{1}0)$ surfaces measured at $h\nu = 68$ eV ($\theta_i = 45^\circ$ and $\theta_d = 0^\circ$ for (0001) and $\theta_i = 60^\circ$ and $\theta_d = 11^\circ$ for $(10\bar{1}0)$). An ARPES spectrum of $\text{Ni}_2\text{P}(0001)$ measured at 76 eV ($\theta_i = 45^\circ$ and $\theta_d = 0^\circ$) is also shown as a gray line. A clear cut-off at the Fermi edge is observed in all the spectra, indicating the metallic nature of Ni_2P . The valence band spectrum of (0001) at $h\nu = 68$ eV is essentially similar to that of $(10\bar{1}0)$ at $h\nu = 68$ eV; a large band which is peaked at 1.3 eV with a shoulder around 2.5 eV is observed at 0–4 eV, and an additional band is observed around 8 eV for both surfaces. The former band is ascribed to a Ni 3d–P 3p hybrid band [2,13], and will be called as a main band, hereafter. The band around 8 eV should be ascribed to a satellite characteristic of PES spectra of Ni and Ni compounds [14–18]. As the spectrum of (0001) is measured at $h\nu = 76$ eV, the main band intensity is increased while the satellite intensity is much suppressed, indicating that the band intensities are substantially dependent on the photon energy. The integrated intensities of the main band and the satellite in PES spectra of $\text{Ni}_2\text{P}(0001)$ are plotted as a function of photon energy in the inset of Fig. 1. The satellite intensity is enhanced at $h\nu = 66$ –75 eV while the main band

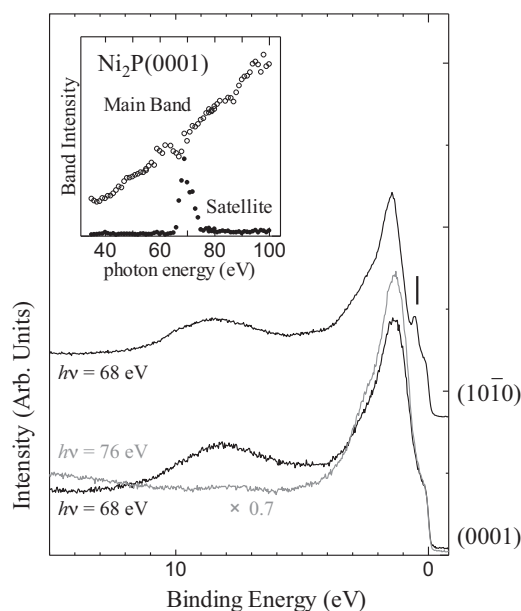


Fig. 1. ARPES spectra of $\text{Ni}_2\text{P}(0001)$ and $(10\bar{1}0)$ measured at $h\nu = 68$ eV ($\theta_i = 45^\circ$ and $\theta_d = 0^\circ$ for (0001) and $\theta_i = 60^\circ$ and $\theta_d = 11^\circ$ for $(10\bar{1}0)$) (black lines) and a spectra of $\text{Ni}_2\text{P}(0001)$ measured at $h\nu = 76$ eV ($\theta_i = 45^\circ$ and $\theta_d = 0^\circ$) (gray line). The inset shows integrated intensities of the main band (open circles) and of the satellite (filled circles) in normal-emission spectra of $\text{Ni}_2\text{P}(0001)$ as a function of photon energy.

intensity shows a dip around $h\nu = 67$ eV. The plots of the intensities of the main band and the satellite in PES spectra for $(10\bar{1}0)$ are essentially identical to those in the inset of Fig. 1 [12]. The satellite intensity is maximized at $h\nu = 69$ eV, which is close to the Ni 3p binding energy (66.7 eV [9]). Therefore, the intensity maximum is interpreted as originating from the resonance arising from the interference between a direct Ni 3d photoemission process and the process induced by the Ni 3p \rightarrow 3d photoexcitation followed by the 3d electron emission through a super-Coster-Kronig decay. The latter process results in a two-hole bound final state, and thus the satellite is associated with the photoemission process leading to the two-hole bound state. The main band is composed of Ni 3d and P 3p components. However, the photoionization cross section of Ni 3d (8 Mb) is much higher than that of P 3p (0.3 Mb) in the present photon energy region [19], and thus the spectral shape of the main band mostly reflects the density of states (DOS) of Ni 3d component. The intensity of the main band is increased with increasing $h\nu$ for the most part, however, the intensity shows a dip around $h\nu = 67$ eV. The intensity of the main band observed in ARPES spectra for $(10\bar{1}0)$ also shows a dip at $h\nu = 67$ eV [12], and thus the dip structure should reflect the $h\nu$ -dependence of the photoionization cross section of the main band. The dip is interpreted as being caused by the fact that the direct Ni 3d photoemission process is competed with the Ni 3p \rightarrow 3d photoexcitation process around the Ni 3p photoexcitation threshold [14]. Therefore, the dip structure is characteristic of the photoionization cross section of the Ni 3d component.

Though the spectral features of the main band and the satellite for $\text{Ni}_2\text{P}(0001)$ and $(10\bar{1}0)$ are essentially identical with each other, there exists a small peak around 0.6 eV only for $(10\bar{1}0)$. The position of this peak is shown by a vertical bar in Fig. 1. The peak is sensitively attenuated by slight Ar^+ ion sputtering (0.5 keV, 1 μA , 5 min) and has no dispersion along the axis normal to the surface [12], and thus the initial state should be ascribed to a surface-localized state. At first glance, these results seem to mean that the state is induced by some surface impurities which are easily removed by Ar^+ ion sputtering. However, no impurity is observed in

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