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# SURFACE STATE OF AMORPHOUS NICKEL PHOSPHIDE FILMS PREPARED BY RF SPUTTERING

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Amorphous nickel phosphide films were prepared by an RF glow discharge sputtering technique. The amorphous nickel phosphide films with various compositions were easily prepared by changing the sputtering atmosphere and below 25 atom%P phosphorus donated electrons to nickel but above 25 atom%P phosphorus accepted electrons from nickel.

Amorphous alloys are well known to have many potential properties which are quite unexpected for crystalline metals. These amorphous materials are usually prepared by quenching very rapidly molten alloys to produce splats or ribbons. An RF (Radio Frequency) sputtering method using a glow discharge is a rather new technique to provide amorphous alloys. Very thin film alloys are prepared by this method and the film thickness is controllable by varying the conditions of the glow discharge. These alloys are supposed to have dangling bonds because of amorphous structure and therefore are expected to be useful catalysts for several reactions.

In the previous paper,$^{1)}$ amorphous nickel boride film alloys were prepared by RF glow discharge sputtering in ($Ar+B_2H_6+H_2$) atmospheres. The amorphous nickel boride films with various compositions (B;0-90 atom%) were easily obtained. Surface state of films was estimated by the XPS Ni 2p3/2 satellite intensity and boron was found to donate electrons to nickel. The product distribution in the hydrogenation of 1,3-butadiene varied with the surface state of nickel. Thus the hydrogenation ability of nickel increased with increasing the electron density of nickel.

Amorphous nickel phosphide films were prepared by the RF sputtering in ($Ar+PH_3+H_2$) or ($Ar+PH_3$) atmospheres. The surface composition of the films was evaluated on the basis of the XPS peak area ratios of the P 2p and Ni 2p3/2 levels. The variations of the surface composition with the partial pressure of ($PH_3+H_2$) or $PH_3$ are shown in Fig.1. Employing $PH_3$ diluted with $H_2$ (5.37 vol%) as a phosphorus source, the phosphorus concentration in the films increased with increasing the ($PH_3$+$H_2$) partial pressure. The phosphorus concentration, however, was not increased above 40 atom% even if the ($PH_3$+$H_2$) partial pressure was set above 0.30 Torr. It was found to be difficult to dope phosphorus in contrast to boron in nickel metal.[1] Employing pure $PH_3$ (99.999%) instead of ($PH_3$+$H_2$) to increase the phosphorus concentration, it steeply increased to 80 atom% at 0.15 Torr.

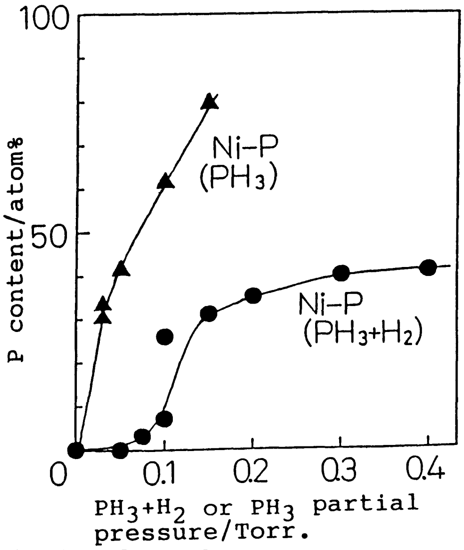

Fig.1. Plot of phosphorus concentration against $PH_3$+$H_2$ or $PH_3$ partial pressure.

X-Ray photoelectron spectra were obtained by using a Shimadzu ESCA750 X-Ray photoelectron spectrometer. All binding energies were corrected by the contaminant carbon (C 1s= 285.0 eV). X-Ray photoelectron spectra of the P 2p and Ni 2p3/2 levels for amorphous nickel phosphide films are shown in Fig.2. In the P 2p levels, two peaks appeared at 133.9 eV and 130.0 eV. The peak at the lower binding energy was assigned to phosphorus interacting with nickel and the higher was phosphorus oxide ($P_2O_5$). With increasing the phosphorus concentration, the former increased and the latter decreased. In the Ni 2p3/2 level, the main peak due to nickel metal appeared at 853.4 eV, accompanying the satellite peaks on a higher binding energy side.

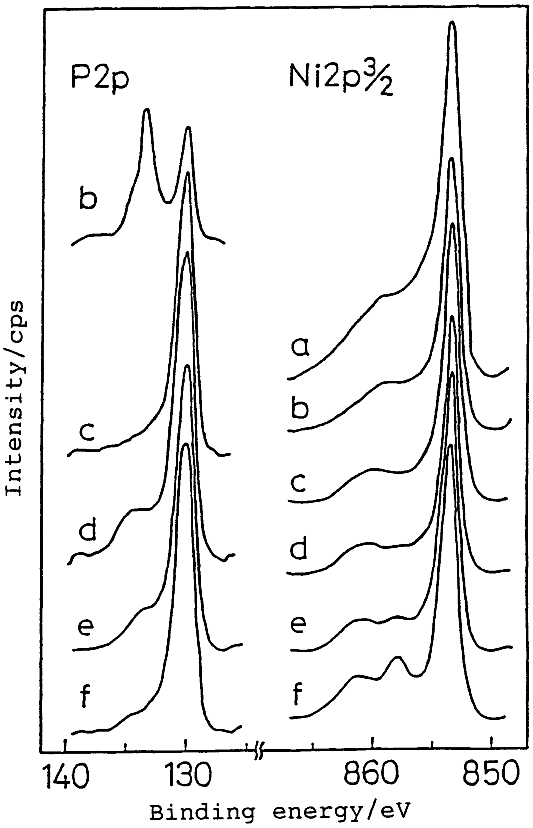

Fig.2. X-Ray photoelectron spectra of P 2p and Ni 2p3/2 levels for amorphous Ni-P films.
a)Ni, b)$Ni_{93}P_7$, c)$Ni_{74}P_{26}$, d)$Ni_{60}P_{40}$, e)$Ni_{39}P_{61}$, f)$Ni_{19}P_{81}$.

The Ni 2p3/2 spectra were separated into five or six Gaussian peaks to reveal the behavior of the satellite peaks of Ni 2p3/2. The synthesized peaks were fit to the original peaks. An example of peak separation for the Ni 2p3/2 spectrum of amorphous $Ni_{38}P_{62}$ film is shown in Fig.3. It was assumed that peaks 1 and 2 were the main peaks and peak 2 was employed to correct the asymmetry of the main peak and that peaks 3, 4, and 5 were assigned the satellite peaks. The peak 5 is attributable to a satellite peak rather than to a nickel oxide peak, because it appears at 857.8 eV. The separations of the satellites from the main peak varied with the phosphorus concentration. Below 25 atom%P, the separations of the peaks 3 and 4 increased with increasing the phosphorus concentration. Above 25 atom%P, they became constant at 8.7 eV and 7.0 eV, respectively. The separations of the peaks 5 and 2 were constant at 4.4 eV and 1.4 eV, respectively, regardless of the phosphorus concentration. The peak 5 thus exhibited obviously a different behavior from the peaks 3 and 4. The satellite peak was divided into two groups, peaks 3 and 4 and peak 5, ($S_h$ and $S_l$, respectively). The satellite intensity($I_{sat}$) and the intensities of $S_h$ and $S_l$ were evaluated by the peak area ratios of the main and satellite peaks($I_{sat}=S_h+S_l$). The dependences of these intensities on the phosphorus concentration are shown in Fig.4. $I_{sat}$ decreased with increasing the phosphorus concentration below 25 atom%P and increased above 25 atom%P. $S_h$ decreased below 25 atom%P and became constant at about 13% above 25 atom%P. But $S_l$ linearly increased up to 60 atom%, while it steeply increased above that concentration of phosphorus. Thus the decrease of $I_{sat}$ below 25 atom%P is due to the decrease of $S_h$, whereas the increase of $I_{sat}$ above 25 atom%P is attributed to the increase of $S_l$. The peak 2, which was introduced to correct the asymmetry of the main peak, was weakened with increasing the phosphorus concentration below 25 atom%P and became constant above 25 atom%P. Thus the main peak became less asymmetric below 25 atom%P.

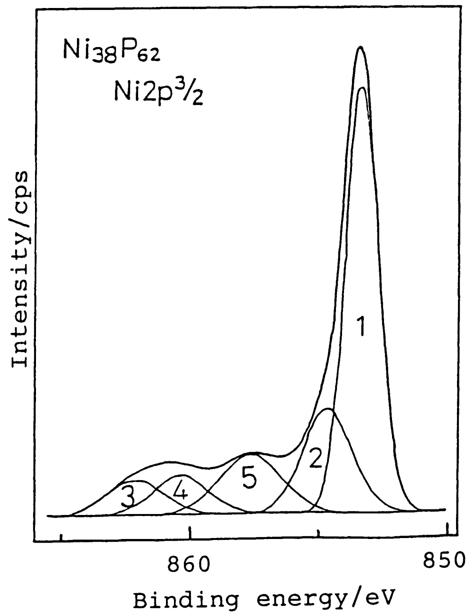

Fig.3. Peak separation of Ni 2p3/2 level for $Ni_{38}P_{62}$ film.

The behavior of the satellite peak of the Ni 2p3/2 spectra was summarized as follows. Below 25 atom%P, $S_h$ was weakened and shifted to a higher binding energy side and the main peak became less asymmetric with increasing the phosphorus concentration.

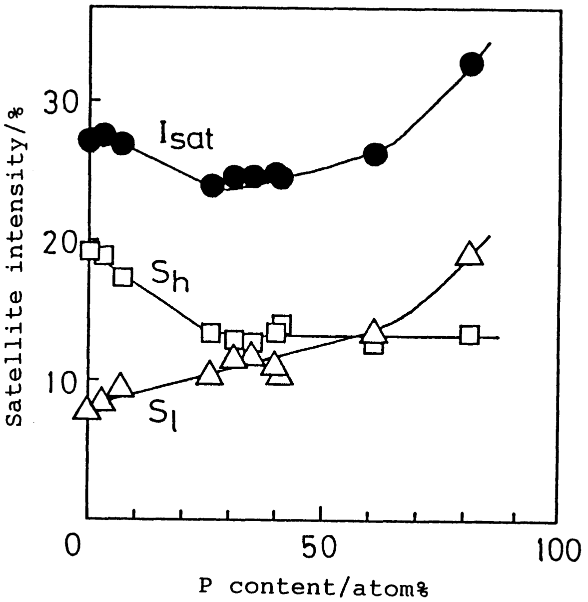

Fig.4. Dependence of $I_{sat}$, $S_h$, and $S_l$ on phosphorus concentration.

These behaviors are similar to those found in nickel boride films.[1] Above 25 atom%P, $S_h$ became unaltered and $S_l$ increased at the same peak position.

The satellite peak of the nickel core level results from the shake up processes in the photoemission.[2-4] The satellite intensity of Ni 2p3/2 spectrum is closely associated with the electron density of the nickel valence band (Ni3d). The decrease of the satellite intensity suggests that the nickel 3d band is partially filled.[5] $S_h$ is assumed to be a shake up satellite. The alterations of $S_h$ and the asymmetry of the main peak below 25 atom%P indicates that the nickel 3d band is partially filled and that the electron density of nickel is increased. $S_l$ is also presumed to result from the intra-atomic excitation of electrons in nickel similar to a shake up process. It is speculated that $S_l$ is enhanced in the presence of phosphorus atom and increases with increasing the phosphorus concentration. Thus, the increase of $S_l$ suggests that the electron density of nickel decreases.

In conclusion, the behavior of phosphorus in the amorphous nickel phosphide films was elucidated. Namely, below 25 atom%P phosphorus donated electrons to nickel and increased the electron density of nickel. Above 25 atom%P phosphorus accepted electrons from nickel and decreased the electron density of nickel. Previously, it has been reported that electrons transferred to phosphorus from nickel in nickel phosphide alloys.[6] These nickel phosphide alloys were prepared by the reduction of the nickel hydroxide using $NaH_2PO_2$ in water and its phosphorus concentration was 40-48 atom%. In this concentration range, the result of the electron transfer is consistent with that of the present study. In addition, the detailed behavior of phosphorus in the wider range was elucidated using the satellite intensity of Ni 2p3/2 spectrum in this report. The investigation of reactivity of amorphous nickel phosphide films is currently under way.

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