An ESCA Study of the Electroless Ni-B Deposits*

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1 Introduction
Sodium borohydride has been successfully used as a reducing agent for electroless plating of nickel. The nickel deposit produced by this method was an alloy of nickel and boron. The Ni-B alloys are characterized by their unusual chemical and physical properties which varied primarily according to the boron content. Therefore, the boron appears to play an important role in determining the physicochemical properties of the Ni-B alloy. After heat treatment, hardness and the other properties of the Ni-B alloy varied in a characteristic manner. It was found that as-plated Ni-B alloy is amorphous, but heat treatment transforms the amorphous structure into a dispersion of Ni,B in a nickel matrix. It is interesting to find out the energy state of boron and nickel before and after the heat treatment to account for the changes in physicochemical properties of the Ni-B alloy. An X-ray photoelectron spectroscopic measurement is useful for the analysis of binding energies of elements in the compound. Therefore, the X-ray photoelectron spectroscopy and X-ray diffraction method were employed to investigate the correlation between the structural features of the Ni-B alloy and binding energies of Ni and B.

2 Experimental
An electroless nickel plating bath of the following composition was used to prepare a Ni-B alloy: 0.04 M NiCl₂, 0.16 M C₂H₆O₂Na₂, 0.75 M NH₄Cl, 1.0 M NaOH, 5 mM NaBH₄. Boron content in the nickel deposit was determined by means of alkaliometric titration of boric acid complexed with mannitol. Ni-B alloys and related samples examined in the present study are shown in Table 1. Photoelectron spectra were measured on an AEI ES-100 photoelectron spectrometer with Al Kα X-ray radiation. All samples except for powdery one were sputtered with argon for 10 ~ 30 min at 20 mA emission current. Binding energies were corrected by using the value of 285.0 eV for C ls electron observed in the background spectrum. X-ray diffraction patterns were measured by the conventional method by use of Co Kα radiation filtered with Fe.

Table 1 Ni-B alloys and related samples tested

<table>
<thead>
<tr>
<th>No.</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nickel plate (99.9%)</td>
</tr>
<tr>
<td>2</td>
<td>Metallic boron (99.5%)</td>
</tr>
<tr>
<td>3</td>
<td>Ni-B alloy prepared by the electroless plating method</td>
</tr>
<tr>
<td>4</td>
<td>Electroless plated Ni-B alloy annealed in H₂ atmosphere at 400°C for 1 hr</td>
</tr>
<tr>
<td>5</td>
<td>Boron powder settled on nickel plate and annealed in H₂ atmosphere at 100°C for 5 hr</td>
</tr>
<tr>
<td>6</td>
<td>H₃BO₃ cryst. (99.5%)</td>
</tr>
</tbody>
</table>

3 Results and Discussion
X-ray diffraction measurements were carried out to investigate the crystallographic feature of the nickel deposit containing about 5% B. In X-ray analysis of the as-plated Ni-B alloy no diffraction line could be detected, which indicated that the material was amorphous. The Ni-B alloy annealed at 400°C for 1 hr and another sample prepared by metallurgical technique under hydrogen atmosphere gave rise to the diffraction lines of Ni,B and Ni as shown in Fig. 1. It is concluded that the Ni-B film produced by the electroless plating method has an amorphous structure, and then changes to the mixture of Ni,B and Ni by the
Fig. 1 X-ray diffraction patterns (Co Kα) of the Ni-B alloys

heat treatment. The photoelectron spectra of Ni 2p½,¾ are shown in Fig. 2. In this case, all samples tested were sputtered with argon to erode the original surface before measurement. The binding energy of genuine nickel was found to be about 853.3 eV. The binding energy of Ni 2p½,¾ in all the other samples took the identical value as that in genuine nickel. Therefore, it may be said that the binding energy of Ni 2p½,¾ did not change by the heat treatment of the electroless Ni-B film. Photoelectron spectra of B ls in the Ni-B film, metallic B, nickel boride prepared by metallurgical technique and boric acid are shown in Fig. 3. The binding energy of B ls in metallic B and boric acid was found to be 187.4 eV and 193.5 eV, respectively. The binding energy of B ls in the as-plated Ni-B alloy was found to be 188.2 eV, but changed to 194.2 eV by the heat treatment. The lower binding energy of B ls corresponds to the metallic B. Therefore, it is believed that boron in the as-plated deposit has a metallic state in amorphous structure. The increment of the binding energy of B ls by the heat treatment was confirmed to be 6.0 eV. Similar result was obtained in the case of nickel boride prepared by metallurgical technique. This chemical shift between the amorphous and crystallized Ni-B alloy can be evaluated by adding the ionic shift (ΔE_{ion}) and the crystal field shift (ΔE_{cryst}),

\[ \Delta E = \Delta E_{ion} + \Delta E_{cryst} \]  

(1)

The ionic shift can be estimated by the electric charge in peripheral orbitals when a chemical bond is formed. If electronic charges are removed from a valence shell the potential
energy of the inner electrons is lowered, and binding energy of the B ls electron becomes larger. In fact, binding energy of B ls in boric acid was higher than that of metallic boron by amount of 6.1 eV. To check whether metallic boron (99.5%) in amorphous structure was oxidized to boric acid or not by a trace amount of absorbed oxygen, heat treatment was carried out in the hydrogen atmosphere at 400°C for 1 hr. Any detectable change was not observed in the ESCA spectral line of B ls after the heat treatment. This finding suggests that the oxidation of boron does not take place under these conditions. The chemical shift observed in the heat treated Ni-B film might be correlated to the formation of the nickel boride (Ni,B). From the viewpoint of the electronegativity, the electron transfer from boron to nickel can not be expected. It was reported, however, that electron transfer will occur from boron to nickel in a nickel-rich boride such as Ni3B to tighten the crystal lattice\(^1\), in which boron atom was isolated from the neighboring borons. The positive charge induced by the electron transfer was localized on the isolated boron atom, and thus, binding energy of B ls became larger. On the other hand, the absence of the change in the binding energy of Ni 2p\(_{3/2}\) before and after the heat treatment will be explained by the following reason. The electron transferred from boron will be delocalized on the nickel lattice to tighten the crystal. Therefore, the ionic shift in Ni-B system may be canceled out by the crystal field force. These ideas described above fully explain the behavior of the ESCA spectra of Ni 2p\(_{3/2}\) and B ls before and after the heat treatment. On the basis of the X-ray analysis and ESCA spectra of the electroless Ni-B deposit, it was found that amorphous Ni-B alloy gave rise to crystalline Ni3B and Ni by the heat treatment, and binding energy of B ls increased by amount of 6.0 eV under these conditions.

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References:
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