Fe–Ni–B alloy thin films were prepared by using an electroless plating method, and their thermal-expansion behavior, thermal-stress generation, and crystal structure were evaluated. By heating from 30 °C to 300 °C, the electroless-plated Ni–5 wt% B alloy film showed a marked increase in tensile stress at approximately 270 °C, which is caused by a phase separation from the amorphous Ni–B alloy into a highly crystalline Ni and Ni3B compound. The coefficient of thermal expansion (CTE) of electroless-plated Ni–B alloy film from 300 °C to 30 °C, after heating to 300 °C, was 14 ppm/K. In contrast, the electroless-plated Fe–Ni–B alloy film in the Invar composition range had a small CTE (8 ppm/K to 9 ppm/K) and no substantial change in crystal structure during heating to 300 °C. As a result, the Fe–Ni–B alloy film on the silicon substrate (CTE = 3 ppm/K) exhibited a lower thermal stress compared with the electroless-plated Ni–B alloy film. Thus, it is suggested that the electroless-plated Invar Fe–Ni–B alloy films are suitable as an under-bump metal layer from the viewpoint of the thermal-expansion behavior.

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The miniaturization and higher functionality of electronic devices has led to an increasing demand for the high-density packaging of semiconductor devices.7 To meet the demand, a metal thin-film forming process, i.e., an under-bump metal (UBM) layer coating for chip bumping and cap metal forming for Cu interconnect applications, has been focused. Electroless Ni-plating methods enable parallel processing of plural wafers as metal thin-film forming, and it has the advantage of being economical.6 Electroless-plated Ni–P alloy films that exhibit a slow growth rate of intermetallic compound with the solder and a good solder wettability have been used widely as the UBM layer. In addition, electroless-plated Ni–B alloy films have a superior solderability compared with electroless-plated Ni–P alloy films because their thin oxide layer can be penetrated by the solder.7,8 Thus, electroless-plated Ni–B alloy films have also received attention in the Cu interconnect technology because they act as a diffusion barrier layer to prevent Cu diffusion.9 Environmental awareness has led to the wide use of lead-free high-temperature solders, such as SnAgCu or SnAg.10 Because the lead-free soldering leads to an increase in the reflow temperature and an increase in the Sn ratio in the solder, with respect to the Ni–P alloy, an interdiffusion among the solder and the Ni–P alloy causes, and thus a decrease in bonding strength arises frequently.10–12 A high thermal stress of the electroless-plated Ni–P alloy films will be generated during the high-temperature reflow process, and reliability problems are a concern.12 Furthermore, the coefficient of thermal expansion (CTE) of the Ni–P alloy is 12 to 13 ppm/K,13 which is a mismatch with that of the silicon semiconductor of 3 ppm/K.14 For these reasons, a new electroless-plated film is desired as a UBM material with a high reliability instead of the conventional electroless-plated Ni–P alloy film.

Electroless-plated Fe–Ni–B alloy films exhibit an excellent wettability and a low reaction rate with lead-free solders compared with electroless-plated Ni–P alloy films.15,16 The Fe–Ni–P alloy films are thus promising as a highly reliable UBM material. The CTE of the Fe–Ni alloy can be adjusted by the Fe content of the alloy (CTE: 1 to 13 ppm/K).17 The CTEs of the Fe–Ni alloys with an Fe content from 55 wt% to 70 wt% Fe are smaller than that of Fe (CTE = 12 ppm/K)17 or Ni (CTE = 13 ppm/K).17 The Fe–Ni alloy with 64 wt% Fe exhibits the lowest CTE (approximately 1 ppm/K) among the Fe–Ni alloys.17 These Fe–Ni alloys with 55 wt% to 70 wt% Fe are termed “Invar alloys”.17 The Invar Fe–Ni alloy has attracted researcher interest15,16,18,19 because of the possibility of reducing the thermal stress by matching the alloy’s CTE with that of silicon and other substrates for integrated circuit packaging. However, the thermal-expansion properties and structural changes of the electroless-plated Fe–Ni–P alloy films during annealing, and which will be associated with the thermal-stress generation, have not been studied.

In this study, we produced electroless-plated Fe–Ni–B alloy films in the Invar composition range using dimethylamine borane (DMAB) as a reducing agent at a lower process temperature than that used for electroless plating of Ni–P alloy system, because the electroless plating process used in electronic applications requires a relatively lower process temperature.20 Most electroless Fe–Ni–B alloy plating studies reported to date have used Ni-rich alloys with Fe contents of approximately 20 wt%, i.e., magnetic permalloys.21–23 Thus, studies focused on electroless plating with the Invar composition range, and using DMAB have not been published.

We prepared Fe–Ni–B alloy films with various alloy compositions via electroless plating, and investigated the thermal-expansion properties of the obtained films. In particular, the thermal expansion and stress behavior of the films were studied with a change in crystal structure up to 300 °C in consideration of the high-temperature reflow process.

Experimental

To prepare an electroless Fe–Ni–B alloy film, a plating bath and plating conditions were devised as shown in Table I. The reagents used were chemical-grade products that were manufactured by FUJIFILM Wako Pure Chemical Corporation and Nacalai Tesque. Iron-sulfate heptahydrate and nickel-sulfate hexahydrate were used as the metal-ion source. Citrate, which is widely used for electroless plating, was selected as the main complexing agent.24,25 Pyrophosphate was used as a pH buffer agent in the electroless-plating bath in the alkaline range because the pKa of pyrophosphate is 9.4.26 A small amount of pyrophosphate is known to form insoluble complex ions in the pyrophosphate solution with an excess concentration of Ni and Fe ions.25,26 However, in this study, it is believed that precipitates, such as insoluble complex ions do not exist in the prepared electroless-plating bath, and all metal ions form soluble complex ions because a large amount of citrate is added as the main complexing agent. As reported...
by Ishikawa et al., it is thought that citrate–pyrophosphate mixed complexes are formed. We used DMAB as the reducing agent. DMAB is a boron compound with a smaller impurity co-deposition rate in the film, that is derived from the reducing agent, than the phosphorus compound as a reducing agent. A pure Cu sheet in contact with an Al sheet was used for the substrate, with reference to the results of Zhou et al. The total metal-ion concentration was 0.05 mol/L, and the ratio of Fe\(^{2+}\)/Fe\(^{3+}\) was varied from 0 to 0.4. The bath temperature was 70°C, the pH was 10.0, and the plating time was 1 h.

The composition of the obtained electroless-plated Fe–Ni–B alloy film was measured using an electron-probe microanalyzer (EPMA, JXA-8230 JEOL Ltd.) at a 15 kV acceleration voltage and a beam diameter of 20 μm, with ZAF correction. The thickness of the plated film was determined by using the fluorescence X-ray-FP method (SEA6000 VX, Hitachi High-Technologies Corporation). As standard samples, a pyrometallurgically produced Fe–Ni alloy (Kojundo Chemical Lab. Co., Ltd.) was used. The grain size was calculated from the grain largeness observed from field-emission scanning-electron microscopy (FE-SEM, JEOL Ltd. JSM-6700F) images of the surface of the electroless-plated film.

Stress measurements were performed with varying temperature, and based on the results, the thermal expansion of the plated film was evaluated. For the accurate measurement of sample warpage, a flat 4-inch-diameter silicon (Si) wafer was used (approximately 525 μm thickness), and a measurement sample was prepared onto which an examining film was plated. This allowed for an accurate measurement of the thermal stress of the plated film on the substrate. Ni–Cr seed layers (thicknesses of approximately 10 nm) were sputtered onto the Si wafer; the Ni seed layer was allowed to contact an Al sheet and the examining film was electroless-plated uniformly. The plated-film thickness was approximately 500 nm so that the sample warpage from heating could conform to the Stoney equation. By using a laser interferometer (FLX-2320S, Toho Technologies), the curvature (R) of the sample was changed from 30°C (assumed as room temperature) to 300°C, which is the high reflow temperature at 1°C/min in N\(_2\) (500 mL/min). The obtained curvature was calculated as the thin-film stress (σ) by using the Stoney Equation.

\[
\sigma = E_s \cdot t_s^2 / [6(1 - \nu_s) R \cdot t_p]
\]

where σ is the thin-film stress, \(E_s\) is the Young’s modulus of the substrate, \(t_s\) is the thickness of the substrate, \(t_p\) is the film thickness, \(\nu_s\) is the Poisson’s ratio of the substrate, and \(R\) is the curvature. \(E_s(1-\nu_s)\) is the biaxial elastic modulus of the substrate. For the biaxial elastic modulus of Si, 180.5 GPa was applied.

First, the stress value \(\sigma_{\text{NiCr}}\) of the Ni and Cr sputtered layers as intermediate layers was measured, then, electroless-plated Fe–Ni–B films were deposited onto the substrate, and the stress \(\sigma_{\text{FeNiCr}}\) measured. The stress \(\sigma_{\text{film}}\) of the electroless-plated Fe–Ni–B alloy film was obtained by subtracting \(\sigma_{\text{NiCr}}\) from \(\sigma_{\text{FeNiCr}}\), based on Equation 2. A change in stress from 30°C to measurement temperature \(T\) was defined as \(\Delta \sigma_{\text{thermal}}\), based on Equation 3. Finally, the CTE, \(\alpha\), of the electroless-plated Fe–Ni–B alloy film was calculated from Equation 4.

\[
\sigma_{\text{film}} = [\sigma_{\text{total}}(t_{\text{NiCr}} + t_{\text{film}}) - \sigma_{\text{NiCr}} \cdot t_{\text{NiCr}}] / t_{\text{film}}
\]

\[
\Delta \sigma_{\text{thermal}} = \sigma_{\text{film}}(\text{at measurement temperature } T) - \sigma_{\text{film}}(\text{at } 30°C)
\]

\[
\alpha_{\text{film}} = \frac{(\Delta \sigma_{\text{thermal}} / \Delta T) \cdot (1 - \nu_{\text{film}})}{E_{\text{film}} + \alpha_s}
\]

where \(t_{\text{film}}\) is the Ni and Cr film thickness as an intermediate layer; \(t_{\text{film}}\) is the film thickness of the electroless-plated Fe–Ni–B alloy film; \(\sigma_{\text{film}}\) is the CTE of the electroless-plated Fe–Ni–B alloy film; \(\alpha_s\) is the CTE of the substrate Si (3 ppm/K). The value measured with a nano-indentation hardness tester (ENT-2100, Elionix Inc.) was used; both Poisson’s ratios were set to 0.3.

The structure of the electroless-plated film was examined using an X-ray diffractometer (XRD, Rigaku Co., CuKα ray, 40 kV, 250 mA, continuous scan, thin-film method, X-ray incident angle 2°). To calculate the full width at half maximum (FWHM) value of the strongest peak, XRD peak fitting was performed using the pseudo-Voigt function.

**Results and Discussion**

 Alloy composition, deposition rate, surface morphology, and crystal structure of electroless-plated Fe–Ni–B alloy films. Figure 1 shows the alloy composition and the deposition rate of the electroless-plated Fe–Ni–B alloy film obtained from the plating bath, where the ratio of Fe\(^{2+}\)/Fe\(^{3+}\) was varied from 0 to 0.4.

An electroless-plated Ni–B alloy film that contained approximately 5 wt% boron (B) was obtained from the plating bath without Fe\(^{2+}\) addition. When Fe\(^{2+}\) was added to the bath, the Ni and B contents of the resulting film decreased gradually, and the Fe content increased to 70 wt%. When the Fe\(^{2+}\)/Fe\(^{3+}\) ratio was 0.2 or more, the B content was less than 0.3 wt% and hardly detectable. When the Fe\(^{2+}\)/Fe\(^{3+}\) concentration ratio was 0.3 or more, electroless-plated Fe–Ni–B alloy films in the Invar composition region were obtained. Matsuoka et al. reported that, compared with an electroless-plated Ni–B alloy film, an electroless-plated Fe–Ni–B alloy film with an increased Fe film content allowed the B content that was incorporated into the film to decrease as the DMAB oxidation rate decreased. In the electrochemical co-deposition of Fe and Ni, Ni is deposited preferentially because its reduction–oxidation potential is more noble; \(E' = (\text{Ni}^{2+}/\text{Ni}) = \text{−}0.23 \text{ V}\) and \(E' = (\text{Fe}^{2+}/\text{Fe}) = \text{−}0.44 \text{ V}\). Thus, it is difficult to increase the Fe content in the electroless-plated films. Zhou et al. reduced the difference in reduction potential between...
Fe$^{2+}$ and Ni$^{2+}$, by using ethylene diamine tetraacetic acid (EDTA) whose stability constant of the complex with Ni$^{2+}$ is larger than that of the complex with Fe$^{2+}$, and obtained an electroless-plated film with an Fe content of 97 at%. They reported that the addition of EDTA narrowed the difference in reduction potentials between Fe$^{2+}$ and Ni$^{2+}$, calculated using the Nernst equation, by approximately 54 mV compared with the aquo-ions.\textsuperscript{15}

The reduction potentials of each complex ion in the case of citrate addition was calculated. Because the pK$\alpha$ of citrate is 5.69,\textsuperscript{37} it existed as cit$^{-}$ at pH 10. The stability constants of the complexes, $K_{\text{Ni-cit}}$ and $K_{\text{Fe-cit}}$, are, with common logarithm values ($\log K_{\text{Ni-cit}}$ and $\log K_{\text{Fe-cit}}$) at 20°C, reported\textsuperscript{37} to be 4.4 and 5.4, respectively. As a result of calculations, the difference in reduction potentials between the Fe$^{2+}$ and Ni$^{2+}$ decreased by approximately 20 mV, which shows a slight narrowing. Zhou et al.\textsuperscript{15} believe that because the electroless-plating reaction is carried out at a higher pH and temperature, the difference in reduction potentials decreases more and Fe deposition is promoted during the actual electroless-plating reaction.

Ohno et al.\textsuperscript{25} reported that when Fe and Ni were electroless-plated simultaneously in alloy electroless-plating reaction, the reduction potentials of the metals, and in particular, the reduction of Fe, shifted to a more noble potential compared with each single-metal electroless-plating bath.

We added pyrophosphate to buffer the electroless-plating solution’s pH. Without pyrophosphate, the pH decreased from 10 to 9.5 after electroless-plating for 1 h, and the Fe content of the electroless-plated film was 36 wt%. A precipitate formed in the bath after a few hours. In contrast, when pyrophosphate was added, the pH decreased from 10 to only 9.8 after electroless-plating for 1 h. Even after several hours, no precipitate formation was confirmed. Therefore, the addition of a small amount of pyrophosphate to the electroless-plating bath improved the stability of the alkaline (pH 10) electroless-plating bath. It is believed that the formation of an Fe and Ni complex with citrate decreased the difference in reduction potential that resulted with a higher Fe content in the alloy films. In future studies, a detailed electrochemical examination is required for Fe and Ni electroless co-deposition under various conditions.

The deposition rate of the film decreases with an increasing Fe$^{2+}$ concentration in the bath. As indicated by many researchers,\textsuperscript{21,38,39} this occurs because the alloying of Fe reduces the catalytic activity, i.e., the degree of reactivity of the oxidation reaction of a B-containing reducing agent on the Fe–Ni–B alloy. According to Kita,\textsuperscript{41} the hydrogen-exchange current density on Fe is smaller than that on Ni. The lower catalytic activity on Fe compared with Ni is believed to result from the slow dehydrogenation reaction of the reducing agent, which is the first electroless plating reaction.\textsuperscript{41}

The surface morphologies of the obtained films are shown in Figure 2. All films were dense continuous films without cracks. In the Ni–B alloy film without Fe, the grain size was so fine that it could not be measured, but in the Fe–Ni–B alloy-plated films with Fe contents from 15 wt% to 40 wt%, as the Fe content increased, the grain size increased from 10 nm to 30 nm. In the Fe–Ni–B alloy-plated film with an Fe content of 60 wt%, which corresponds to the Invar composition, the grain decreased slightly (it was approximately 10 nm as observed with a transmission electron microscope, results not shown), and in the Fe–Ni–B alloy-plated film with an Fe content of 70 wt%, the grain size increased again from 50 nm to 100 nm. In contrast, the diameter of the agglomerates of these grains was approximately 100 nm for any film.

The relationship between the grain diameter and the composition of these electroless-plated Fe–Ni–B alloy films will be described in detail and will be correlated with the XRD results.

Figure 3 shows the XRD patterns of the as-deposited electroless Fe–Ni–B alloy films with varying Fe contents. When a Cu sheet was used as the substrate in electroless plating, a strong Cu diffraction peak was detected. As a result, it was difficult to identify the diffraction peak of the electroless-plated film. Thus, to evaluate the crystal structure of the electroless-plated Fe–Ni–B alloy films, a Ni/Cr/Si substrate was used, which was also suitable for measuring the film stress.

The electroless-plated Ni–5 wt%B alloy film showed a broad diffraction pattern. According to the literature,\textsuperscript{12,41} the electroless-plated Ni–B film exhibits ultrafine crystals when the B content is 4 wt% or less, whereas when the B content exceeds 4 wt%, the Ni–B films become amorphous. The obtained Ni–5 wt%B films are presumed to be amorphous from the results of previous research\textsuperscript{12,41} and XRD examination. Conversely, distinct diffraction peaks derived from the face-centered cubic (fcc) phase were observed in the diffraction patterns of the Fe–Ni–B alloy-plated films with Fe contents of 15 wt% to 55 wt%. The FWHM of the fcc (111) peak at approximately 44° decreases from 7° to 0.9° with increasing Fe contents from 5 wt% to 55 wt% in the Fe–Ni–B alloy-plated films. By increasing the Fe
content, a higher film crystallinity resulted. For the Fe–Ni–B alloy-plated film with a high Fe content of 64 wt%, a body-centered cubic (bcc) (110) peak was detected on the higher-angle side in the vicinity of 44° along with the fcc (111) peak. That is, a mixed bcc and fcc phase was observed in the film with an Fe content of 64 wt%, unlike the fcc single phase of the pyrometallurgically produced Fe–36 wt% Ni alloy. In the Fe–Ni–B alloy-plated film with a higher Fe content of 70 wt%, a bcc single-alloy phase was observed to be the same as the alloy phase of the pyrometallurgically produced Fe–30 wt%Ni alloy.

With respect to the crystal structure of the pyrometallurgically produced Fe–Ni alloy produced through an ordinary melting-solidification process, it is difficult to indicate clearly the composition boundary between the fcc and bcc structure of the Fe–Ni alloy. In general, the following facts have been reported:42–45 Fe–Ni alloys from pure Ni up to an Fe content of approximately 67 wt% exhibit an fcc single phase, the Fe–Ni alloys with an Fe content of approximately 68 wt% to 69 wt% show a mixed bcc + fcc phase, and the Fe–Ni alloys with an Fe content of 70 wt% or more have a bcc single phase.

According to the report by Anthony et al.45 for the electroless-plated Fe–Ni–B alloy film obtained from a citrate–ammonium-lactate bath, an fcc single phase is present in the Fe–81 wt% Ni–B (< 1%) alloy film, whereas there is a dual-phase alloy of fcc + bcc phase in the Fe–37 wt% Ni–B (< 1%) alloy film. Furthermore, as described in the report of Zhou et al.39, the Fe–Ni–P (< 0.6 wt%) alloy film obtained from a citrate–EDTA bath through the electroless plating method showed an fcc phase in the alloy film with an Fe content of 25 wt%. However, the electroless-plated Fe–Ni–P alloy films with an Fe content of 55 wt% to 70 wt% were proved to be a bcc phase.14 Thus, it has been reported that the crystal structure of the electroless-plated Fe–Ni–B alloy films in the Invar composition range (Fe content of 50 wt% to 70 wt%) contain a metastable bcc phase different from the thermal-equilibrium phase of an fcc single phase.

To date, with respect to the formation of a metastable bcc phase in the electroplated Fe–Ni alloy in the Invar composition range, several mechanisms related to hydrogen generation and hydride formation during electroplating have been proposed,46 however, we have yet to discover the details of such mechanisms. It has been reported that hydrogen generation and hydride formation during the Invar alloy electroplating generate high-density structural defects, which may induce a metastable bcc structure.46 Similarly, in this study of electroless Fe–Ni Invar alloy plating, a metastable bcc phase was probably formed by hydrogen generation and secondary hydride formation, because a noteworthy amount of hydrogen bubbling was observed during electroless Fe–Ni–B alloy plating with an Fe content of 64 wt%.47,48

In Fe–Ni alloy electroplating, the grain size tends to be of the order of several tens of nanometers, although the absolute grain size depends on the bath composition and the plating conditions.49–52 As the Fe content increases, the grain size of the plated film decreases and the smallest grain size is shown in the mixed-phase region of the fcc and bcc phases in the Invar composition.3,15 In the case of single-phase bcc, it has been reported that the grain size increases as the Fe content increases.51,52 Because of the difference in atomic radius between Fe and Ni, a lattice strain is generated when Fe is mixed into the Ni matrix phase or when Ni is mixed into the Fe matrix phase. When a certain extent of dislocation is reached, a grain boundary is formed in the plated film and the grain size of the film becomes finer.49 Moreover, grain growth is difficult in mixed-phase Fe–Ni alloy electroplated films, and because of the mutual formation of crystal phases of the fcc and bcc phase, the obtained film is finer.52

Conversely, it is known that when the electroless-plated Ni film contains B with an atomic radius that differs significantly from that of Ni, the grain diameter of the obtained film becomes finer. A larger B content yields smaller crystal grains. The Ni–B alloy system can become amorphous when the B content in the alloy is approximately 4 wt% or more.42,43

The crystal grain diameter of the electroplated Fe–Ni–B alloy film, with up to 55 wt% Fe content, increased with an increase in Fe content. This is attributed to the decrease in B content in the alloy film. That is, although B contributes significantly to the film micronization compared with that of Fe as an alloying element, the B content decreased because of a decrease of oxidation of DMAB on the Fe-rich Fe–Ni–B alloy-plated film.

For a film Fe content of 64 wt%, it is believed that there was almost no influence on film micronization by co-deposition of B, because of a significantly decreased B content. In contrast, micronization by the solid dissolution of Fe atoms into the fcc Ni matrix phase, and crystal-growth suppression because of mixed bcc and fcc phase states resulted as exhibited by a fine grain with a diameter of approximately 10 nm. In the Fe–Ni–B alloy-plated film with an increased Fe content of 70 wt%, the obtained grain size was considered to increase, because the B content is small and grains grow only in the bcc phase.

**Thermal-expansion behavior and stress generations of electroless-plated Fe–Ni–B alloy films.—** Stress generation during formation of the electroless-plated films.—The stress value σthin of the electroless-plated Fe–Ni–B alloy film from 30 C to 300 C was measured, and from these results, the thermal-expansion behavior of the film was also investigated. Figure 4 shows the stress value (σthin) of an electroless-plated Ni–B alloy film and an electroless-plated Fe–Ni–B alloy film with an Fe content of 55 wt% and 63 wt%, respectively, which are expected to show lower CTEs than those of Ni-rich alloy films, when heated from 30 C to 300 C and cooled from 300 C to 30 C.

Table II shows the calculated CTEs from the change in thermal stress, Δσthin/ΔT, in Figure 4, from 30 C to 70 C of the plating-bath temperature, 200 C and 300 C, which are assumed to be the reflow temperature. The Young’s modulus required for the CTE calculation was measured by using a nanoindenter.

The Young’s modulus values of as-deposited electroless Ni–5 wt%B and Fe–Ni–B alloy films with an Fe content of 55 wt% and 63 wt%, were 200 GPa, 160 GPa, and 150 GPa, respectively. Compared with the Young’s modulus of pyrometallurgically produced Ni (220 GPa), the electroless-plated Ni–B alloy film showed a small Young’s modulus. In contrast, the electroless-plated Fe–Ni–B alloy film gave almost the same value as that obtained from the pyrometallurgically produced Fe–Ni alloy (158 GPa and 151 GPa, respectively).53 Shen et al.54 proposed a rule-of-mixtures model to explain the correlation between the Young’s modulus and the grain size. In this model, a significant decrease in Young’s modulus was observed at grain sizes of 5 nm or less. In this study, the Young’s modulus is smaller than that of the pyrometallurgically produced Ni because the electroless-plated Ni–5 wt%B alloy film comprises an amorphous phase according to an observation of the surface morphology and XRD pattern. It was confirmed that the electroless-plated Fe–Ni–B alloy film contains a larger grain, thus, the same Young’s modulus value is shown as in a pyrometallurgically produced alloy.
In some reports, the stress at room temperature is stated, thus, the obtained stress at 30°C was also described here. At 30°C, the stress of the electroless-plated Ni-5 wt% B alloy film was approximately 130 MPa before heating. The stress of the Fe-Ni-B alloy-plated films with an Fe content of 55 wt% and 63 wt% showed an almost identical tensile stress of 480 MPa and 460 MPa, respectively, which was larger than that of the electroless Ni-5 wt% B alloy film. With respect to the Fe-Ni-B alloy-plated films, there was no significant change in the stress during heating from 30°C to 70°C. At 70°C, i.e., the film-forming temperature, the stress of the Ni-5 wt% B alloy film decreased to 10 MPa and exhibited almost no stress, and the stresses of the Fe-Ni-B alloy-plated films with an Fe content of 55 wt% and 63 wt% were 430 MPa and 410 MPa, respectively.

The stress generated by film formation of the electroless and electroplated films has been reported frequently to depend on the crystal structure and grain size. In electroless-plated Ni-B and Ni-P alloy films, films with a low B or P content derived from a reducing agent are known to have a high crystallinity and tensile stress, which is generated through coalescence with adjacent atoms (crystal coalescence theory).55 When the B content ranges from 0.4 wt% to 1.2 wt%, a value of approximately 300 MPa to 500 MPa is shown at around room temperature.56 If the content of B and P increases further, the value of tensile or compressive stress decreases because amorphization occurs and the atomic rearrangement disappears.56 Vicenzo46 reported that for crystalline electroplated Fe-Ni alloy films, a finer grain diameter yields a higher defect density, which results in a high stress during film formation.

The obtained electroless-plated Fe-Ni-B alloy film has a structure with a crystallinity and fine grains. As a result, because of the mechanism of the crystal-coalescence theory,55 the tensile stress is higher than that in the electroless-plated Ni-B alloy film with an amorphous structure.

**Effect of heating and cooling on the stress of the electroless-plated films.**—As shown Figure 4, the stress σ_film of the Fe-free Ni-5 wt% B alloy-plated film decreased linearly from 130 MPa to −190 MPa with a temperature increase from 30°C to 150°C. In this case, the CTE from 30°C to 70°C was approximately 13 ppm/K, which was the same value as the CTE of pyrometallurgically produced Ni (CTE = 12.9 ppm/K).57 The stress from 150°C to 260°C showed a constant value of −190 MPa, and no change in thermal stress with a variation of temperature was observed. Therefore, the CTE from 30°C to 200°C of the electroless-plated Ni-5 wt% B alloy film decreased to approximately 9 ppm/K. The stress increased significantly to 200 MPa from 260°C to 270°C, which suggests that rapid contraction of the plated film occurred in this temperature range. During heating from 270°C to 300°C followed by cooling to 30°C, the stress increased again and decreased linearly, and reached 1000 MPa at 30°C after cooling. The CTE in heating from 30°C to 300°C decreased to approximately 4 ppm/K, because of the rapid increase in tensile stress at approximately 270°C. The CTE from 30°C to 300°C was 14 ppm/K during cooling, which was close to that of pyrometallurgically produced Ni of approximately 13 ppm/K.57

In contrast, the stresses of the electroless-plated Fe-Ni-B alloy films with an Fe content of 55 wt% and 63 wt% were 450 MPa and 470 MPa at 30°C, respectively, and decreased linearly until approximately 320°C. Therefore, these stress values continued to decrease, although the inclination of the stress curve was reduced slightly until 300°C. When cooling from 300°C to 30°C, these stresses increased linearly and were approximately 600 MPa at 30°C. As a result, the CTE of the electroless-plated Fe-Ni-B alloy films with an Fe content of 55 wt% and 63 wt% showed slightly lower values along 30°C to 200°C and 30°C to 300°C ranges than those between 30°C and 70°C. The CTE from 30°C to 70°C and the CTE at cooling from 300°C to room temperature (30°C) was approximately 9 ppm/K in the Fe-Ni-B alloy-plated film with a 55 wt% Fe content, which is lower than that of the Ni-B alloy-plated film and nearly the same as the CTE of 7.1 ppm/K of the pyrometallurgically produced 55 wt% Fe-45 wt% Ni alloy. In contrast, the CTE of the Fe-Ni-B alloy with an Fe content of 63 wt% was approximately 10 ppm/K, which is smaller than the CTE of the electroless-plated Ni-B alloy film, but nearly 10 times larger than the CTE (1.2 ppm/K)57 of the pyrometallurgically produced Fe-36 wt% Ni alloy of the same composition as the Fe-Ni-B alloy film. However, the CTE values of the electroless-plated Invar Fe-Ni-B alloy films showed the same value as those of the electroplated Invar Fe-Ni alloy that we already reported, namely, approximately 9 ppm/K.58 Details will be described later.

From the above results, the stress value during the formation of the electroless-plated Fe-Ni-B alloy film with the Invar composition was relatively large compared with the electroless-plated Ni-B alloy film. However, the stress change (Δσ_film) of the electroless-plated Fe-Ni-B alloy film was small, because the CTE difference between Si and the electroless-plated Fe-Ni-B alloy film with the Invar composition is smaller than that between Si and the electroless-plated Ni-B alloy film. Therefore, as a result, the film stress σ_film after heating and cooling was σ_film(FeNi) (600 MPa) < σ_film(Ni) (1000 MPa). Therefore, from the viewpoint of thermal-expansion behavior, it appears that the electroless-plated Fe-Ni-B alloy film in the Invar composition range can be used as an UBM layer, which is suitable for high-temperature reflow.

**Table II. CTE of the electroless-plated Fe–Ni–B alloy film.**

| Alloy composition | CTE 30 to 70°C ppm/K | CTE 30 to 200°C ppm/K | CTE 30 to 300°C ppm/K | CTE 300 to 30°C ppm/K |
|-------------------|----------------------|-----------------------|-----------------------|-----------------------|
| Ni-5 wt% B        | 13.4                 | 9.2                   | 3.9                   | 14.3                  |
| Fe-45 wt% Ni-B (<0.3 wt%) | 8.5              | 8.1                   | 7.5                   | 9.3                   |
| Fe-37 wt% Ni-B (<0.3 wt%) | 9.2              | 8.8                   | 8.4                   | 10.2                  |

Effect of heating on crystal structure of electroless-plated Fe-Ni-B alloy films.—To investigate the change in thermal stress of the obtained electroless-plated Fe-Ni-B alloy films during heating and cooling, the impact of film composition on the CTE value and the effect of heat-treatment on the crystal structure of the films was evaluated by XRD. In addition, the surface morphology was observed before and after heating.

Figure 5 shows the XRD pattern of the electroless-plated Fe-Ni-B alloy films with an Fe content of 0 wt%, 55 wt%, and 63 wt%, before and after stress measurement up to 300°C. Figure 6 shows the X-ray diffraction patterns of the films in the as-deposited state and after heating to 300°C. Figure 7 shows the XRD pattern of the films in the as-deposited state and after heating to 300°C. In contrast, the surface morphology of the films in the as-deposited state and after heating to 300°C was almost the same. Moreover, after heating, no crack was observed in the surface morphology.

In general, Ni-B alloys obtained through the electroless-plating method exhibit different crystallization behaviors during annealing, depending on their B content and heating rate. In most cases,
Figure 5. Effect of heating on crystal structure of electroless-plated Fe–Ni–B alloy films. a) as-deposited Fe–5 wt%Ni, b) annealed Fe–5 wt%Ni at 300 °C, c) as-deposited Fe–45 wt%Ni–B (< 0.3 wt%), d) annealed Fe–45 wt%Ni–B (< 0.3 wt%) at 300 °C, e) as-deposited Fe–37 wt%Ni–B (< 0.3 wt%), f) annealed Fe–37 wt%Ni–B (< 0.3 wt%) at 300 °C.

However, in heat-treatment from approximately 270 °C to 300 °C, an amorphous Ni–B alloy phase undergoes phase separation to a crystalline Ni matrix and Ni₃B compound. At the phase separation, the alloy phase transforms from a low-density amorphous phase to the crystal phase, in which the atomic filling density increases. In this study, it is assumed that the electroless-plated Ni–B alloy film showed a sharp increase in stress because of the contraction of the plated film at 270 °C, which is caused by the phase transformation accompanied by densification. Song et al. reported that the tensile stress increases rapidly in the electroless-plated Ni–P alloy film because of the formation of Ni₃P through heating at approximately 300 °C. Furthermore, as in our experience, they observed a gentle decrease in stress during heating, before a sudden increase in tensile stress. They explained that this phenomenon results from the recovery of defects and grain growth. In this study as well, because the same behavior is observed at approximately 200 °C by heating the electroless-plated Ni–B film, recovery may have occurred, which is a preliminary stage of phase separation.

Conversely, the XRD pattern of the electroless-plated Fe–Ni–B alloy film shows an fcc single phase at an Fe content of 55 wt% in the as-deposited film, as described above, and a mixed bcc phase and fcc phase with respect to the film with an Fe content of 63 wt%. After heating at 300 °C, a slight decrease in the FWHM of the crystal-phase peak and an increase in the fcc peak height at approximately 43° were observed. The peak at approximately 30° is derived from the formation of a thin oxide film on the film surface. Although a slight oxidation of the film surface was observed from the surface-morphology inspection after heating at 300 °C, as a result of heating, it was very similar to the as-deposited film, and no crack was observed. However, the grain sizes of the plated films with Fe contents of 55 wt% and 63 wt% were approximately 10 nm in the as-deposited film, and after heating at 300 °C, they were approximately 20 nm. A slight increase in grain sizes was observed after heating. In this case, the gradient of thermal stress became gentle near 220 °C and the stress value increased to 600 MPa at 30 °C after cooling. This suggests that recovery may occur, as in the case of the electroless Ni–B alloy film. The appearance of minute borides, not observed in the XRD pattern, is also conceivable, because of a trace amount of B of less than 0.3 wt%, and the possibility of an increase in lattice-filling density, because of poor grain growth.

In an Fe–Ni alloy in the Invar composition range, including the bcc phase prepared through electroplating, phase transformation from the bcc phase to the fcc phase and plated film contraction, caused by heat-treatment at 400 °C or higher, were observed. The electroplated Fe–Ni alloy film that contained the ferromagnetic bcc phase with a high saturation magnetization (Bs) shows a smaller thermal expansion than Ni alone, however, it exhibits a larger CTE than that of the low Bs antiferromagnetic fcc single-phase Fe–Ni alloy. It has also been reported that the CTE of the electroplated film can exhibit Invar properties of a low CTE by transforming from the metastable bcc phase and fcc phase to the same fcc single phase as the pyrometallurgically produced material through heat-treatment, accompanied by film contraction caused by structural densification. Therefore, the electroless-plated Fe–Ni–B alloy film with an Fe content of 63 wt% that contains the bcc phase, obtained in this study, showed a higher CTE than that of the pyrometallurgically produced alloy of the same composition. A comparison with reported CTE values of electroplated Fe–Ni alloy films without B shows that these CTE values did not differ from those of electroless-plated Invar alloy films. B, which is a characteristic impurity in electroless-plated films, existed at less than 0.3 wt% in the electroless-plated Invar alloy films, and so, it is believed that B did not affect the CTEs and the crystal phase that is related closely to the CTEs. The phase transformation from bcc to fcc did not occur at 300 °C, as well as in the electroplated Invar alloy film. Therefore, it can be considered that there was no sudden increase in tensile stress caused by densification during heating to 300 °C, unlike in the electroless-plated Ni–B alloy film.

Figure 7 summarizes the results above schematically. The effects of heating and cooling on electroless-plated Ni–B and Fe–Ni–B alloy films are as follows.

In the electroless-plated Ni–B alloy film, the crystal structure of the as-deposited film is amorphous. As such, the stress before heating is small. By heating, a large tensile stress is generated because of contraction through phase separation from the low-density amorphous phase into crystalline Ni and Ni₃B. Furthermore, because the matrix phase was Ni with a large CTE of approximately 14 ppm/K, the change in thermal stress from heating and cooling was large. Therefore, the stress σₓₓₓ of electroless-plated Ni–B alloy film after heating and cooling was large at 1000 MPa. Conversely, the electroless-plated Fe–Ni–B alloy film with an Fe content of 55 wt% and 63 wt% had a
B content of as low as 0.3 wt%, compared with the electroless-plated Ni–5 wt%B alloy film, and the film is highly crystalline with a large grain diameter. As such, the tensile stress of the as-deposited film is large to some extent, and the tensile stress increases only slightly because of the non-formation of the B-phase compound during heating to 300 °C. Film contraction did not occur, and because the Fe–Ni–B alloy film was of the Invar composition, the CTE was approximately 8 ppm/K to 9 ppm/K which is close to that of Si, thus, the stress change because of heating from 30 °C to 300 °C and cooling to 30 °C is considered to be small. The electroless-plated Fe–Ni–B alloy film with an Fe content of 63 wt% contains the metastable bcc phase, but no phase transformation to the fcc phase occurred at 300 °C, which is assumed to be a high-temperature reflow temperature, and thus, a high thermal stability resulted.

Conclusions

We prepared Fe–Ni–B alloy thin films by using the electroless plating method, and their thermal-expansion behavior, thermal-stress generation, and crystal structure were evaluated. The following was concluded.

The Fe–Ni–B alloy-plated film with an Fe content of 0 wt% to 55 wt% showed an fcc single phase. In contrast, the Fe–Ni–B alloy-plated film with an Fe content of 63 wt% showed a mixed metastable bcc phase and an equilibrium fcc phase. The Fe–Ni–B alloy-plated film with a Fe content of 70 wt% showed a bcc phase. The Fe–Ni–B alloy-plated film with an Fe content of 63 wt% gave the same value as the CTE of the pyrometallurgically produced Ni and the pyrometallurgically produced Fe–45 wt%Ni alloy, of 14 ppm/K and 8 ppm/K, respectively. The CTE of the electroless-plated Fe–Ni–B alloy film with an Fe content of 63 wt% was 9 ppm/K, which is different from that of the pyrometallurgically produced alloy of the same composition. The crystalline structure of the metastable bcc phase is different from the pyrometallurgically produced alloy.

It is suggested that the electroless-plated Fe–Ni–B alloy film in the Invar composition range had a small CTE and no substantial change in crystal structure during heating to 300 °C. As a result, the Fe–Ni–B alloy film on the silicon substrate exhibited a low thermal stress compared with the electroless-plated Ni–B alloy film. It is thus suitable as a UBM layer from the viewpoint of thermal-expansion behavior.

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Figure 7. Schematic diagram showing effects of heating and cooling on stress, crystal structure, and CTE of electroless-plated Ni–B and Fe–Ni–B alloy films.
