The structural and electrical properties of electroless nickel-boron thin films.

Patty Tung. Dubois

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THE STRUCTURAL AND ELECTRICAL PROPERTIES OF ELECTROLESS NICKEL-BORON THIN FILMS

by

Patty Tung Dubois

A Thesis Submitted to the Faculty of Graduate Studies through the Department of Physics in Partial Fulfillment of the Requirements for the Degree of Master of Science at the University of Windsor

Windsor, Ontario 1974
ABSTRACT

An electron microscope study supplemented by electrical resistivity measurements has been performed on electrolessly deposited Nickel-Boron thin films. Three kinds of pretreatment were employed. They are (i) conventional; (ii) conventional with improved sensitizer; (iii) catalytic. The temperature of the Nickel-Boron metalizing bath was 60°C. The effect of increasing the deposition temperature (up to 95°C) was also studied. The film thickness ranged from 300 Å to 1,000 Å. The boron content was 5.7 percent by weight (w/o). The study of electron microscopy and resistivity measurements was done in both the as-deposited state and the annealed state. The samples for annealing were vacuum heated to 400°C. In contrast to the Nickel-Phosphorus system, the islands of the Nickel-Boron system show characteristic internal structure. The resistivities of Nickel-Boron are consistently higher than that of Nickel-Phosphorus both before and after the annealing.
The author would like to express her appreciation to Dr. M. Schlesinger and Dr. N.E. Hedgcock for their continued interest and advice throughout this work.

The author wishes to express her gratitude to Dr. A. van Wijngaarden for his permission to use the necessary equipment for the experimental part of this work.

Thanks are due to Mr. B. Sears and Mr. G. Berthiaume for their skillful technical assistance. The continuous help of Mr. S.L. Chow and Mr. A. Okoniewski is also gratefully acknowledged.

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CHAPTER I

INTRODUCTION

1.1 Thin Films

A thin film is simply a layer of material of thickness usually less than 1 um. It has a very large ratio of surface to volume. Due to the fact that the atoms at the surface are not surrounded on all sides by similar atoms as are interior atoms, a surface may have quite different properties from the bulk of the material underneath. A thin film, only a few dozen atoms thick, might be regarded as "all surface". Consequently, its properties may be quite different from those of the bulk material. In fact, this is generally so, especially for the physical properties. Thus, thin films provide a completely new field of physics and chemistry.

Because of their wide commercial use and application, thin films have been studied extensively for over a century. Practical applications include electrical circuits, superconducting devices, optical instruments, magnetic information devices, etc.. With rapid technological advances in the preparation of films, thin films are expected to draw considerable attention in the future.
There are many ways to prepare a thin film. Vacuum Evaporation, Electrodeposition, Chemical Reduction, Vapor Plating, Anodization, Sputtering, and Electroless Plating are the most common methods used today.

1.2 Electroless Thin Films

Electroless plating was first discovered by A. Brenner and G.E. Riddell in 1946 (1). The name "electroless" was given because no electrodes or external energy source was required, in contrast to other chemical deposition methods. Following the success of electroless deposition of Nickel and Cobalt from Brenner's baths, Gold, Silver, Chromium, Iron, Copper, Palladium, and Antimony were electrolessly deposited (2). Recently, many commercial processes have been developed employing the electroless plating technique. Some firms, for instance, are making use of electrolessly deposited nickel films on ceramic as a resistor material. In the plating of plastics, this technique is also most commonly used, since it is the most economic and easiest way to plate onto a dielectric substrate.

Generally speaking, electroless plating is a controlled autocatalytic chemical reduction process for metal deposition. That is, the metal ions in the plating solution are converted to neutral atoms by a reducing agent in the solution, but
this process is restricted to the substrate to be coated due to a chemical reaction which needs catalysis by a fresh metal surface; each depositing layer of the film is catalysed by the preceding layer. The major components of the metal solution contain metal salt, reducing agent, complexing agent, buffer and stabiliser. The complexing agent prevents metal precipitation by forming complex metal ions which do not form insoluble salts with the reducing anions present in the bulk of solution. However, they are still capable of being reduced on the catalytic surface. The buffer keeps the pH value of the solution constant during the chemical reduction. The role of the stabiliser is either (i) to protect the active catalytic nuclei from reaction with impurities, or (ii) to adsorb on to the surface of colloidal impurities, preventing metalization on the colloidal particles rather than on the desired catalytic surface.

In order to effectively deposit metals using the electroless plating technique, a pretreatment of substrates is essential. Substrates after pretreatment act as catalysts for initiating the deposition; then the deposition is carried on autocatalytically.

One of the more prevalent procedures, the conventional system, is the two-step immersion sequence of acidic stannous chloride solution followed by an acidic palladium chloride
solution. The first bath is generally referred to as the "sensitizer", and the second the "activator" (3,4). Another widely used procedure, the catalytic system, is the immersion of a catalytic solution (via palladium chloride in excess acidic stannous chloride) followed by "acceleration" (hydrochloric acid or sodium hydroxide). The former is usually named "catalyzer", and the latter "accelerator". In the review of literature concerning the electroless system, most investigators (e.g., 4,5,6,7) devoted attention to the conventional system with almost complete omission of the catalytic system. Only recently, some attempts have been made to elucidate the mechanism of the catalytic system (8).

The net result of these pretreatments is the net formation of the fine nuclei involving palladium, which act as the catalytic centers to initiate the plating process (4,5). It has been demonstrated that the nucleation and growth of the electroless thin film is initiated at these catalytic sites.

In some recent publications, it has been shown (9,10,11) that the effectiveness of conventional tin sensitizing solution may be improved greatly by either adding aged (at least one week) stannic chloride to the conventional solution, or using it in a separate step prior to the immersion in the conventional solution. An improvement in the sensitizing performance was also found (12) through the aging of diluted acidic stannous
chloride for one to two weeks. Direct evidence (13) came from the comparative study of the transmission electron micrographs in the different stages of the plating process between the conventional sensitizer and the improved sensitizer based on the incorporation of an aged stannic chloride component.

1.3 Electroless Nickel-Boron Thin Films

Alternatives to hypophosphite ions as reducing agents in electroless nickel solution have been investigated by various workers in the field. Alkali metal borohydrides and alkyl amine boranes (borazanes) are those of the few which have had some success (14, 15). On examination, one finds a distinct analogy between these and the hypophosphites. They both react with water to produce hydrogen, and the metallic nickel deposited by the borohydride anion (BH₄⁻) contains boron whereas nickel deposited by the hypophosphite anion (H₂PO₂⁻) contains phosphorus.

Although some suggestions have been made about the electroless nickel solutions by using borohydrides or amine boranes as the reducing agent (16, 17, 18, etc.), the available literature concerning the mechanism of nickel-boron plating is rather limited, and proposed ideas are not confirmed by experimental data. A survey of early work has been given by Goldie (2). Investigations have been carried out on the
deposition chemistry, differential thermal analysis, X-ray diffraction, mechanical properties, and magnetic properties (19,20,21,22,23) of electroless nickel-boron thin films.

This work describes further studies of electroless nickel-boron thin films (23), involving electron microscopy and measurements of electrical resistivity. Results are presented for both freshly deposited and vacuum heat treated films prepared under different conditions. Some results are also compared with those obtained from the earlier work on the electroless nickel-phosphorus system (4,24).
CHAPTER II

EXPERIMENTAL PROCEDURE

The methods and apparatus used in the present experimental work are discussed below.

2.1 Preparation of Film Specimens

Ni-B thin films used for electron microscopy were grown on Formvar substrates, and for electrical measurements were grown on microslide glass substrates.

2.11 Substrate Cleaning

Glass substrates were first wiped with "Kimwipes", then washed in a special detergent for glass. After being rinsed well in distilled water, they were cleaned in chromic acid-sulfuric acid solution (200 gm chromic acid + 75 ml sulfuric acid + 400 ml distilled water) at a temperature of about 80°C for half an hour, and finally rinsed again in distilled water. The freshly cleaned, wet substrates were used immediately for film depositions.

Formvar (4 gm polyvinyl formal in 1 l ethylene dichloride) was freshly coated on mechanically wiped glass
microslide substrates from its solution, and therefore did not require any special cleaning.

2.12 Substrate Activation

Three different kinds of premetalizing chemical paths were employed for the electron microscopy investigations. They were (a) Conventional sensitizer (fresh SnCl₂/HCl) and activator (PdCl₂/HCl) (b) Improved conventional with (i) aged SnCl₄ (at least one week at room temperature) added to fresh conventional sensitizer or (ii) aged conventional sensitizer (4 to 6 days) and activator (c) Catalytic with Shipley 9F (catalyzer) and 19F (accelerator) solutions(8). The properties of these solutions have been investigated previously (8,12,13). For the electrical measurements, only pretreatment of the Improved type (aged conventional sensitizer and activator) was chosen in order to obtain homogeneous, finely deposited specimens.

The compositions of "stock" solutions and working solutions are listed in table I. The working solutions are always freshly prepared from the stock solution.

The cleaned substrates were immersed in the sensitizer (or catalyzer) for 2 min. at room temperature, and rinsed in distilled water for 15 sec.. They were then immersed in the activator (or acclerator) for another 2 min., and rinsed again
TABLE I

Compositions of Stock Solution and Working Solution

<table>
<thead>
<tr>
<th>Stock Solution</th>
<th>Working Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SnCl₂</strong> solution 10gm</td>
<td>Sensitizer 1ml SnCl₂/100ml H₂O</td>
</tr>
<tr>
<td>HCl 10ml</td>
<td></td>
</tr>
<tr>
<td><strong>PdCl₂</strong> solution 1gm</td>
<td>Activator 1ml PdCl₂/200ml H₂O</td>
</tr>
<tr>
<td>HCl 10ml</td>
<td></td>
</tr>
<tr>
<td>H₂O 100ml</td>
<td></td>
</tr>
<tr>
<td><strong>SnCl₄</strong> solution 0.65M</td>
<td>Improved Sensitizer:</td>
</tr>
<tr>
<td></td>
<td>(i) (1mlSnCl₂ + 1mlSnCl₄)/100ml H₂O</td>
</tr>
<tr>
<td></td>
<td>(ii) 1ml SnCl₂/100ml H₂O aged</td>
</tr>
<tr>
<td></td>
<td>for 4-6 days at room temp.</td>
</tr>
</tbody>
</table>

in distilled water for 15 sec. also at room temperature.

2.13 Electroless Nickel-Boron Deposition

After catalyzation, the substrates were dipped into the electroless nickel-boron plating solution, whose composition is given in Table II. The metalizing bath was the same that was
given as "B" by Gorbunova et al (23). It employs borohydride as the reducing agent, and contains no stabilizer. The pH value of the Ni-B solution was read from a Beckman Digital pH meter.

| TABLE II |
| Composition of Ni-B Plating Bath |

<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Chloride (NiCl₂)</td>
<td>30 g/l</td>
</tr>
<tr>
<td>Sodium Borohydride (NaBH₄)</td>
<td>1.2 g/l</td>
</tr>
<tr>
<td>Sodium Hydroxide (NaOH)</td>
<td>40 g/l</td>
</tr>
<tr>
<td>Ethylene Diamine (H₂NCH₂CH₂NH₂) (100%)</td>
<td>60.2 ml/l</td>
</tr>
<tr>
<td>pH value</td>
<td>14</td>
</tr>
</tbody>
</table>

It has been known (2) for some time that alkali metal borohydrides (e.g. NaBH₄) react spontaneously with aqueous solutions of nickel salts to form a precipitate of black nickel boride, Ni₂B. The oxidation of borohydride ions by water is very rapid in acid and neutral solution. For these reasons, the NaOH was dissolved first, followed by NaBH₄ and H₂NCH₂CH₂NH₂. NiCl₂ was dissolved separately in a second
beaker. By mixing the two parts together, a stable Ni-B metalizing was then made. Of course, the dissolution of either part must be complete.

In order to deposit Ni-B films at higher than room temperature (60°C to 95°C), a Thermomix Junior Immersion Thermalstat was employed to control the temperature of a large water bath, into which a beaker containing the Ni-B solution was placed. The temperature of the plating bath was thus stabilized to within 0.5°C. The Ni-B solution is rather unstable and deteriorates rapidly once spontaneous decomposition starts. Only a few samples could be prepared in each fresh batch of solution. Generally, the deposition time was used to determine the film thickness.

2.14 Vacuum Heat Treatment of Films

An evacuated quartz or glass tube wound with resistance wire was used as a small furnace for the heat treatment of films. The tube containing samples was first flushed with dry nitrogen gas three times, then evacuated to about 10⁻⁵ Torr. The samples were heated up from room temperature to 400°C with constant heating rate of 10°C/min. They were kept at 400°C for 45 min., then cooled down to room temperature at the same rate of about 10°C/min.

The vacuum system was always maintained at the pressure
less than $10^{-5}$ Torr. The heating current was controlled manually, while the temperature was monitored by a Copper-Constantan thermocouple. (for example, see Ref. 25). A simple diagram of the vacuum heat treatment system is given in Fig. 1.

2.2 Electron Microscopy of Films

As mentioned before, the Ni-B thin films were electrolessly deposited on Formvar substrates. The coated Formvar layer was subsequently floated off the glass microslide in distilled water, and placed on copper specimen grids for insertion into the electron microscope. (see Fig. 2)

The as-deposited (fresh) thin discontinuous Ni-B specimens with different chemical pretreatments were studied under the electron microscope, and micrographs were made. Some of those samples were then heat treated, as described in 2.14, and examined once again under the electron microscope. This was done immediately after the vacuum annealing.

The transmission electron micrographs and the selected area electron diffraction patterns of Ni-B films before and after the annealing were studied and compared. An aluminum foil standard was used to calibrate the measurements of diffraction patterns. The electron microscope used here
FIGURE 1: Schematic Diagram of Heat Treatment System.
FIGURE 2: Preparation of Specimen Grids
for Electron Microscope Investigation.
is a Hitachi HU-12 operated at 100 KV.

The electron microscope is in principle very much like the conventional microscope. It consists of an electron gun and an assembly of electron lenses as shown in Fig. 3. This depicts schematically the ray paths in a microscope employing three stages of magnification and a double condenser lens system for illuminating the specimen. The specimen to be examined by transmission of electrons is placed near the entrance of the objective lens. The magnified image produced by the objective lens and the first projector lens is called the intermediate image. This serves as an object for the second projector lens which produces the final magnified image on the fluorescent viewing screen.

Fig. 3a illustrates the mechanism of production of

![Diagram](image-url)
FIGURE 3: The Basic Structure of Transmission Electron Microscope.
contrast on transmission micrograph. The illuminating beam of electrons is scattered by the specimen. In the case of crystalline materials, this scattering takes the form of Bragg diffraction. An aperture is inserted in the objective lens as shown in Fig. 3a. It does not allow Bragg reflections to pass through to the final image, which is therefore mainly formed by the direct transmitted beam. This type of image is called a "bright-field" image. The contrast is thus produced by differences in intensities of electrons scattered into Bragg reflections from various parts of the thin specimen. As a result, hills and valleys on the original surface are made to appear as regimes of dark and light contrast on the fluorescent screen.

Image can also be formed by any one diffracted beam by either displacing the aperture to receive this beam, or by tilting the illumination so that the required beam passes down the axis of the object. The resulting image is known as a "dark-field" image. It then reveals which regions of the specimen are contributing to the diffracted beam. Consequently, these regions of the specimen are seen as regimes of light contrast from a dark-field image.

The fundamental principles of electron diffraction are analogous to that of X-ray diffraction. The condition is usually expressed by Bragg's Law of diffraction:
\[ n \lambda = 2d \sin \theta \]

where \( n \) is an integer (the order of reflection), \( d \) is the spacings between atomic planes, \( \theta \) is the Bragg angle measured between ray and plane, and \( \lambda \) is the wavelength of the incident electron. Experimentally, for randomly oriented polycrystals, \( d \) spacing value can be obtained using the following equation based on the assumption of small angles scattering:

\[ d = \frac{2L\lambda}{D} \]

where \( L\lambda \) is the diffraction constant of the electron microscope, \( D \) is the diameter of the diffraction ring.

More details of the electron microscope can be found in a number of texts. (Ref. 44, 45, 46)

2.3 Electrical Measurements

The D.C. resistivity of Ni-B thin films was measured by the four-probe method due to van der Pauw (26) as follows. The resistivity \( \rho \) of a homogeneous, isotropic metal film with constant thickness \( d \) but arbitrary shape is given by

\[
\exp \left( -\frac{\pi d}{\rho} R_{AP, CD} \right) \cdot \exp \left( -\frac{\pi d}{\rho} R_{BC, DA} \right) = 1 \tag{1}
\]
where

\[ R_{AB,CD} = \frac{V_D - V_C}{I_{AB}} \quad \text{and} \quad R_{BC,DA} = \frac{V_A - V_D}{I_{BC}} \]

A, B, C, D are four different point contacts at the periphery of the film. \( I_{AB} \) is the current measured between contacts A and B; \( V_D - V_C \) is the voltage measured between D and C etc.

For these measurements, deposition was made directly onto microscope slide glasses. Circular samples were subsequently made by placing the deposited glass in a Teflon mask, and etching away the unwanted Ni-B with a dilute solution of HCl and HNO\(_3\). Spring loaded stainless steel contacts were located on the periphery of the circular samples for the measurements. The diagram of the sample holder is shown in Fig. 4.

To minimize the asymmetry and to correct the geometry of the samples, the whole circuit for resistivity measurements was designed so that the contacts of the voltage and the current can be interchanged. The polarity of the input voltage is also reversible. \( R_{AB,CD} \), as well as \( R_{BC,DA} \), was then taken from the average of the four measurements.

Theoretically, when the sample possesses a line of symmetry, \( R_{AB,CD} \) should be equal to \( R_{BC,DA} \) (see Ref. 26).
FIGURE 4: Schematic Diagram of the Sample Holder for Resistivity Measurement.
Experimentally, only those samples with the ratio of \( \frac{R_{AP,CD}}{R_{BC,DA}} \) or \( \frac{R_{BC,DA}}{R_{AP,CD}} \) less than 5 were chosen, as conforming to the circular symmetry of the samples. The resistivity of the sample was then calculated from Eq. (1) for the known thickness d. The circuit diagram for the D.C. resistivity measurements is shown in Fig. 5.

The resistivities of Ni-B films with various thicknesses (less than about 1,000 Å) were determined both before and after the vacuum heat treatment. The procedure for annealing was the same as described before, except that a bigger Pyrex heating tube was used. The current in the sample was restricted to 100 µA during the measurements.

For comparison, films of Ni-P of various thickness were also electrolessly deposited at room temperature. Their D.C. resistivities before and after the heat treatment were then measured and compared with those of Ni-B films in the range of thickness less than 1,000 Å. The compositions and pH value of the electroless Ni-P metalizing solution are given in Table III.

2.4 Thickness Measurement

The thickness of the film was measured directly by the
FIGURE 5: Circuit Diagram of D.C. Resistivity Measurement.

S1: Mode R1, R2
S2: Interchange IV, VI
S3: Measure I; V
S4: Polarity Nor, Off, Rev
S5: Current $10^{-3}$, $10^{-4}$, $10^{-5}$
Table III

Compositions of Ni-P Plating Bath

<table>
<thead>
<tr>
<th>Substance</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel Sulfate (\text{NiSO}_4\cdot6\text{H}_2\text{O})</td>
<td>29.1 g/l</td>
</tr>
<tr>
<td>Sodium Hypophosphite (\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O})</td>
<td>17.5 g/l</td>
</tr>
<tr>
<td>Succinic Acid Disodium Salt (\text{NaO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Na})</td>
<td>14.9 g/l</td>
</tr>
<tr>
<td>Succinic Acid (\text{HO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{H})</td>
<td>1.3 g/l</td>
</tr>
<tr>
<td>pH value</td>
<td>5.3</td>
</tr>
</tbody>
</table>

multiple-beam interference method due to Tolansky (27). The instrument used was the Varian A-scope interferometer (model no. 980-4000). A basic schematic diagram is shown in Fig. 6 together with a typical interference image graph.

The spacing of the fringes in the image graph is \(\lambda/2\) which for the Sodium D-lines is 2946 \(\AA\). The film thickness is given by the height of the steps in the fringe pattern in unit of 2946 \(\AA\). The accuracy of the instrument is about \(\pm30 \AA\).
FIGURE 6: Schematic Diagram of Multiple Beam Interferometer together with a Interference Image Diagram.
The specimens required for thickness measurement were first mechanically cut to get a sharp edge, then coated with an opaque vacuum-deposited layer of aluminum about 1,000 Å thick. The thickness of the specimen can be determined from its interference fringe pattern. For details of the multiple beam theory, see Reference (27).
CHAPTER III

THEORY OF ELECTRICAL CONDUCTION

The electrical conductivity of a metal in the free-electron gas theory of Drude-Lorentz-Sommerfeld is treated in standard text books (e.g. Kittel, Ref. 28), and is given by

$$\sigma_0 = \frac{ne^2 \tau}{mv}$$  \[2\]

where \( n \) is the number of free electrons per unit volume, \( e \) is the electronic charge, \( m \) is the effective mass of the electron, \( v \) is the average velocity of the electronic charge at the surface of Fermi distribution, \( \tau \) is the mean free path (mfp) of the conduction electrons.

The generalized conductivity expression deduced from the free electron model in the modern theory consists of an ideal and residual resistance terms. The ideal resistance term given by Eq. [2] is proportional to \( T \) at high temperatures and to \( T^5 \) at very low temperatures (28, 29). The residual resistance part is caused by scattering of the electron wave by impurity atoms which disturb the periodicity of the lattice. If the concentration of impurity atoms is small, this part is found to be independent of temperature (28). However, the
temperature coefficient of resistivity for bulk metals is always a positive constant.

3.1 Continuous Thin Films

When an ideal free electron type metal is thinned to a thickness comparable with its mean free path \( l \), the film boundary (i.e., surface) will impose a geometrical limitation on the movement of the conduction electrons and thus the effective values of the mean free path. This is generally called the "size" effect.

If \( \sigma_f \) is the conductivity of a thin film with thickness \( t \), \( \sigma_B \) the conductivity of the bulk material, \( \gamma \) the ratio of \( t/l \), and \( p \) (0 \( \leq \) p \( \leq \) 1) the scattering coefficient, theoretical variation of \( \sigma_B/\sigma_f \) (by Fuchs and Sondheimer(30)) as a function of \( \gamma \) is shown in Fig. 7 for several values of \( p \). Physically speaking, only a fraction \( p \) of the electrons is scattered elastically from both surface of the film, while the rest are scattered diffusely with complete loss of their drift velocity. The limiting forms of \( \sigma_B/\sigma_f \) given by Fuchs and Sondheimer for thick films (31) are

\[
\frac{\sigma_B}{\sigma_f} = \frac{\rho_f}{\rho_B} = 1 + \frac{3}{8\gamma}(1 - p) \quad (\gamma > 1)
\]
FIGURE 7: Theoretical variation of the film-to-bulk resistivity ratio ($\rho_F/\rho_B$) with normalized thickness $t/\ell$ ($\ell$ is the mfp) for several values of the scattering coefficient $p$. The dotted curves represent the approximate form (Eq. (2)) in the limiting case of $\gamma \gg 1$. 
Equation [3] is also plotted in Fig. 7 as dotted curves. A comparison of the two sets of curves shows that Eq. [3] is sufficiently accurate approximation for values of γ as low as 0.1. If the resistivity values fall above the p=0 curve, the films do not behave according to the theory. Such film behavior may result from discontinuous films, and films whose structure, purity, etc., differ from those of the parent bulk metal.

Another useful relation for the resistivity of films is Matthiessen's rule (32). According to the rule, various electron scattering processes (and hence resistivity contributions) are additive, provided that lattice scattering remains predominant. Therefore

\[ \rho_F = \rho_1 + \rho_2 + \rho_3 + \rho_4 \]

where \( \rho_F \) is the film resistivity and \( \rho_1, \rho_2, \rho_3, \rho_4 \) are component resistivities due to structural imperfection, impurities, phonon scattering (temperature dependent part), and surface scattering (thin film part).

As the film thickness decreases, deviation from Matthiessen's rule is expected because of the size effect. It needs to be emphasized that Fuchs' theory is applicable only to the thickness dependence arising out of the limitation of the free path by the geometrical boundaries.
3.2 Discontinuous Films

It is known that very thin films are discontinuous, consisting of islands (discrete particles). Such films generally have very low conductivity and negative temperature coefficient, and their conductivity does not follow the prediction of the Fuchs-Sondheimer theory. The conductivity is found to vary exponentially with the inverse of temperature, suggesting that the conduction mechanism is thermally activated. Moreover, it is ohmic at low applied fields but nonlinear at high fields. A brief discussion of conduction mechanism of discontinuous films follows.

(1) Thermionic Emission

We know that activation processes occur by means of the emission of charge over a potential barrier, consequently thermionic emission is a likely process of conduction. The activation energy would then be a measure of the height of the potential barrier between particles. When two particles are very close, the height of the barrier may decrease significantly because of the overlap of the image-force potential, thus raising the conductivity. Minn. (33) derived the following expression for conductivity on this basis:

\[ \sigma = \frac{NeT}{k} \exp \left( - \frac{\psi - Be^2/d}{kT} \right) \]  

[4]

where \( A \) is a constant characteristic of each film, \( T \) the
temperature, \(e\) the electronic charge, \(k\) the Boltzmann constant, \(d\) the distance between particles, and \(\psi\) the bulk work function of the metal.

The term \(Be^2/d\) (\(B\) = constant) is the contribution of the image forces. When \(d\) is sufficiently small (i.e. several angstroms), Eq. [4] predicts a conductivity much higher than that actually observed.

(2) Quantum-Mechanical Tunneling

For much smaller particle spacings, it is possible that quantum-mechanical tunneling through the barrier will be dominant. By quantum mechanical tunneling is meant the penetration of thin potential barrier by electrons incident on the barrier. However, this mechanism predicts the transfer current to be relatively temperature independent. (34,35)

(3) Activated Tunneling

Gorter (36) and Darmois (37) introduced a thermal-activation term in the tunneling mechanism by using the activated process involving transfer of charge from one initially neutral particle to another some distance removed. The activation energy \(e^2/\epsilon r = 14.4/\epsilon r\) (\(r\) is the linear dimension of the particle in angstroms, \(\epsilon\) is the dielectric constant) is thus the electrostatic-potential barrier. Only electrons or
holes excited to states of at least this energy from the Fermi level will be able to tunnel from one neutral particle to another. On this basis, Neugebauer and Webb (38) proposed an activated transfer mechanism in which charge carriers created by thermal activation (since \( e^2/r \approx kT \)) over the electrostatic potential barrier are transported by tunneling from one neutral particle to another. They derived the following conductivity expression:

\[
\sigma = d^2 e^2 D \exp\left(\frac{-e^2/\epsilon r}{kT}\right) \quad [5]
\]

\[
= \frac{d\sqrt{h}}{r} \exp\left(\frac{e^2}{\epsilon r kT} - \frac{4\pi d}{h} \sqrt{2m\phi} \right)
\]

where \( D \) is the transmission coefficient, \( h \) is Planck's constant, \( \phi \) is the potential barrier between particles, which can be approximated by the work function of the metal, \( r \) is the linear dimension of particles, \( \epsilon \) is the dielectric constant of the medium surrounding the particles, \( k, T, d \) are the same as mentioned before. From Eq. [5], an ohmic behavior (at low fields) of conductivity, an exponential dependence on reciprocal temperature and a marked dependence on the island size and interisland distance are predicted.

(4) Tunneling via Substrate

The barrier height for free tunneling is of the order
of the work function of the metal, and that for tunneling through a dielectric is much less, being the difference between the work function of the metal and the electron affinity of the dielectric. The reduced barrier height enhances the transmission coefficient. Thus, conduction by tunneling through the substrate is expected to be significant for very thin films. Hill (59,40) has done some work on this basis for the case of very small particles ($\sim 10 \AA$).
CHAPTER IV

EXPERIMENTAL RESULTS AND DISCUSSION

The growth and structure of electroless Ni-B films have not been studied, consequently very little information was available from the literature. As an understanding of film geometry and structure is essential in the study of electrical and other properties of films, the growth and structure of Ni-B films on nonconducting substrates were examined as part of this research. The experimental results lead to some conclusions about the microstructure in connection with the available knowledge of the electroless Ni-P system.

4.1 Electron Microscopy

4.1.1 Fresh Nickel-Boron Thin Films

A representative transmission electron micrograph of a Ni-B thin film deposited at 60°C using conventional sensitizer is shown in Fig. 8a. As we can see, the deposit of Ni-B is composed of islands. This is quite typical of the initial stages of thin film growth in general. The Ni-B islands are
FIGURE 8a: Transmission Electron Micrograph of a Ni-B Thin Film deposited at 60°C using Conventional Sensitizer.

FIGURE 8b: Selected Area Electron Diffraction Pattern of 8a.
circular in shape and of rather uniform size (about 200 Å). The islands show a characteristic "flower-like" internal structure which is significantly different from that of other electroless thin films (e.g. Ref. 4, 5, 6, 7, etc.). The corresponding selected area electron diffraction pattern, shown in Fig. 8b, consists of only a few very broad, diffuse rings indicating a very low degree of order.

Previous studies (4, 41, 42) of electroless Ni-P films (pH=5.3) showed that they were also composed of circular islands of uniform size, but with no discernible internal structure. Selected area electron diffraction gave patterns also having a few broad rings (Fig. 4 of Ref. 4).

In some cases, Ni-B films grown with the conventional sensitizor show an internal structure which has a more "cellular" appearance instead of a "flower-like" structure. One example is shown in Fig. 9a. Fig. 9b is the corresponding electron diffraction pattern. Both types of internal structure have been occasionally seen in the same sample.

This cellular internal structure is the usual result of employing the "improved" sensitizor obtained either by aging the conventional sensitizor or by adding aged stannic chloride to the conventional sensitizor. A typical electron micrograph of a Ni-B film deposited at 60°C with improved sensitizor is shown in Fig. 10a. The diffraction patterns
FIGURE 9a: Transmission Electron Micrograph of a Ni-B Thin Film also deposited at 60°C using Conventional Sensitizer.

FIGURE 9b: Selected Area Electron Diffraction Pattern of 9a.
FIGURE 10a: Transmission Electron Micrograph of a Ni-B Thin Film deposited at 60°C using Improved (with additional aged SnCl₄) Sensitizer.

FIGURE 10b: Selected Area Electron Diffraction Pattern of 10a.
in these cases show sharper rings, some of which can be identified with a face centered cubic structure (see Fig. 10b). It also seems that some islands have merged together to form worm-like chains or clusters.

It should be mentioned that three major experimental difficulties are inherent in the quantitative interpretation of the diffraction patterns. (i) The amount of material present on the surface is very small and consequently the intensity of the pattern is rather low. (ii) The small size of the "crystallites" present results in rather broad rings, limiting the accuracy of measurement to about 1%. (iii) Possibility of enhanced crystallization due to irradiation by the electron beam.

The Ni-B deposits obtained employing improved sensitizer manifest a denser and a more uniform distribution of islands and clusters than those employing conventional sensitizer as seen from Fig. 8a and Fig. 10a. The visual metallic appearance of Ni-B films using improved sensitizer is also more uniform and homogeneous, which agrees with the above observation. In addition, the deposition rate using the improved pretreatment was found to be approximately twice as fast as that using the conventional one for the same deposition temperature.

The electron micrographs of fresh Ni-B films deposited
employing the Shipley 9F & 19F catalytic system appear quite different from those obtained using the conventional system. A typical result is shown in Fig. 11a. The deposit appears to consist of fine grains of size less than about 70 Å. The corresponding diffraction pattern (Fig. 11b) consists of a few broad rings, indicating very fine crystallites. The metallic lustre of deposits obtained using the catalytic system is higher than for those using the conventional system. The deposition rate is about five times faster under the same deposition conditions.

The effect of raising the deposition temperature, i.e. temperature of Ni-B metalizing solution, increased the deposition rate of Ni-B films with both conventional system and catalytic system pretreatment. This result agrees with Gorbunova's observation (23). However, no noticeable structural change can be found in the electron micrographs of the Ni-B system as a function of the plating bath temperature. This is true for all the three different kinds of pretreatment.

4.12 Vacuum Heat Treated Ni-B films

The result of heat treatment of Ni-B films is a deposit consisting of small crystals. Fig. 12 shows (a) freshly deposited Ni-B (b) the same sample after heat treatment at 400°C. It appears that the cellular structure has been
FIGURE 11a: Transmission Electron Micrograph of a Ni-B Thin Film deposited at 60°C using Catalytic System (Shipley 9F & 19F) Pretreatment.

FIGURE 12: Transmission Electron Micrographs of a Ni-B Thin Film deposited at 60°C using Conventional Sensitizer.

(a) Freshly deposited; (b) After Heat Treatment at 400°C.
replaced by crystallites of approximately the same size as the original cells. This trend has been seen in many other samples of which Fig. 12 is a typical example.

Dark field microscopy also clearly shows the presence of crystals of the order of about 300 Å in size. This is illustrated in Fig. 13. Additional evidence for structural change as a result of heat treatment is seen in the electron diffraction patterns corresponding to Fig. 12a, 12b. As we can see from Fig. 14a, 14b, the diffraction pattern after heat treatment reveals a clearly f.c.c. structure with a lattice constant matching that of bulk nickel within the experimental error. Table IV summarizes the lattice parameter derived from Fig. 14b. The lattice constant of bulk Ni is 3.524 Å, and our calculated value is 3.506 Å with a 0.51% error.

<table>
<thead>
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<th>(h k l) plane</th>
<th>(d_{Ni}) (Å)</th>
<th>(d_{expt}) (Å)</th>
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<tr>
<td>(1 1 1)</td>
<td>2.035</td>
<td>2.028</td>
</tr>
<tr>
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<tr>
<td>(2 2 0)</td>
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<tr>
<td>(3 1 1)</td>
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<tr>
<td>(2 2 2)</td>
<td>1.017</td>
<td>1.008</td>
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Table IV
Theoretical & Experimental d-spacings of Nickel (Fig. 12b)
FIGURE 13: Transmission Electron Micrographs of a Ni-B Thin Film deposited at 60°C using Conventional Sensitizer.
(a) in Bright Field Mode; (b) in Dark Field (111) Mode.
FIGURE 14: The Selected Area Electron Diffraction Patterns corresponding to Figure 12.
(a) Freshly deposited; (b) After Heat Treatment at 400°C.
It is known that the initial structure of as-deposited Ni-P films is metastable and liquid like (4, 41, 42). The Ni-P system can be considered as a solid solution of phosphorus in a very fine polycrystalline nickel system. Previous X-ray studies (20, 21, 23) indicate that a similar situation prevails for Ni-B. That is, boron dispersed randomly within the nickel framework.

Heat treatment of Ni-P above 325°C (41) is known to produce two components, face centered cubic nickel and tetragonal Ni₅P. The latter is a fairly good conductor which has an electronic energy band structure remarkably similar to that of nickel (43). The formation of Ni₃B, Ni₂B and other nickel borides has been observed (20, 21, 23) as a result of heat treatment of thick deposits of Ni-B. However, the electron diffraction patterns of the present samples show no evidence of these nickel borides (see Fig. 14b). It seems therefore likely that in the course of our heat treatment of Ni₃B, nickel crystallizes out leaving the boron-rich material dispersed between the crystallites. More details will be discussed later.

4.2 Electrical Resistivity

4.21 Ni-B Films Before and After Heat Treatment
The D.C. resistivity as a function of film thickness for both fresh and vacuum heat treated Ni-B thin films is shown in Fig. 18. A sharp increase in the D.C. resistivity of thinner films is evident for both fresh and annealed states for thickness in both cases below about 500 Å. Upon heat treatment of the samples, an irreversible change in the D.C. resistivity of Ni-B was observed. The heat treatment appears to lower the resistivity of the same film by about two orders of magnitude. It is a somewhat larger change than that reported on Flechon's (20) for films of thickness 1,000 Å.

4.22 Comparison Between Ni-B and Ni-P

Our measured values of the D.C. resistivity in electroless Ni-P films agree closely with those obtained in the previous work by Schlesinger and Karton (see Fig. 5 of Ref. 24). They are also plotted in Fig. 15 for the sake of comparison.

The following observations can be made after comparing the results from Ni-B and Ni-P: (i) Within each system, the effect of heat treatment appears to be a shift in resistivity which preserves the shape of a curve drawn through the experimental points. (ii) The sharp increase in resistivity for thinner films in the fresh state sets in at about 500 Å for Ni-B and at about half this thickness (about 250 Å) for Ni-P. (iii) The change in resistivity as a result of heat treatment
FIGURE 15: Resistivity of films as a function of thickness.

Ni-B: ◇ freshly deposited; ● heat treated at 400°C.

Ni-P: □ freshly deposited; ◆ heat treated at 400°C.
is about two orders of magnitude for Ni-B and about three
orders of magnitude for Ni-P. (iv) The resistivity of Ni-B
is consistently about an order of magnitude higher than that
of Ni-P films for the same thickness in both fresh and annealed
states.

For the deposits considered here, the boron content is
5.7 w/o (21, 23), and the phosphorus content 9.5 w/o (4).
The presence of either element presumably provides additional
scattering centers in the lattice, thus increasing the resis-
tivity above that of pure nickel. (The resistivity of pure
nickel is 6.6 \( \mu \)O cm.) The decrease of the resistivity after
the vacuum heating can be probably caused by the annealing out
of grain boundaries and other defects. It is physically
reasonable since a part of the scattering of the carriers is
proportional to the defect density in the solid.

The fact that the resistivity of Ni-B is consistently
higher than that of Ni-P after the vacuum heat treatment at
400\(^\circ\)C can be attributed to the fact that nickel crystallizes
out during the vacuum heating, leaving boron-rich material
with lower conductivity dispersed between the crystallites.
The form in which the boron is present seems to depend on the
deposition conditions. Addition of a small quantity of TiNO\(_3\)
as a stabilizer to the metalizing bath resulted in the formation
of Ni\(_2\)B even at 310\(^\circ\)C (22, 23). Our bath contained no
stabilizer and the electron diffraction patterns showed nothing other than f.c.c. nickel. In this respect, our results are similar to those of Flechon (20). It may also be significant to point out that Gorbunova et al studied much thicker deposits (30 µm) than ours (less than 1,000 Å). It is also suggestive that although the island size (i.e., film thickness) is about the same for both systems, the rise in resistivity associated with the transition from continuous films to discontinuous films, occurs at a greater thickness for Ni-B films where the islands are separated into cells. If a direct electrical contact between cells has to be made through a "crust" of poorly conducting material, a greater number of such contacts would be required to produce a drop in resistivity. It is possible that the internal structure of the islands shown in the electron micrographs shows such a separation of nickel-rich from boron-rich regions.

The electrical conduction mechanism of both Ni-B and Ni-P thin films is most probably by tunneling between islands. As we can see from the result of resistivity measurements, all the deposits are almost continuous. That is, most islands of Ni-B and Ni-P thin films are more or less merged together, therefore the interisland distances are very small. Consequently, among all the models of electron transfer mechanism, quantum-mechanical tunneling is probably the most predominant one.
CHAPTER V

CONCLUSION

5.1 Summary

The structure and electrical properties of electrolessly deposited Ni-B thin films have been studied and compared to those of electroless Ni-P films. Electron micrographs of both fresh and heat treated films prepared under different premetalizing conditions, and measurements of electrical D.C. resistivity before and after the vacuum heat treatment have been made.

The Ni-B films obtained using conventional sensitizer have been shown to consist of circular islands with a characteristic "flower-like" internal structure, while a more cellular appearance results from employing an "improved" sensitizer. Electroless Ni-P films using conventional sensitizer were known (4) to consist of the circular islands without internal structure. The Ni-B deposits obtained using the Shipley 9F & 19F catalytic system was found to be fine grained with a particle size less than 70 Å and of rather homogeneous appearance.

The selected area diffraction patterns of as-deposited
Ni-B were all diffuse and broad, indicating a very low degree of order. Upon vacuum heating, the initial cellular structure was replaced by crystallites of about the same size as the original cells. Moreover, the corresponding diffraction pattern after heat treatment showed a clearly f.c.c. structure with a lattice constant matching that of bulk nickel within the experimental error.

The D.C. resistivity of electroless Ni-B was more pronounced in the fresh state than the heat treated state. This is similar to the behaviour of the resistivities of electroless Ni-P from a previous study (24). In addition, the D.C. resistivities of Ni-B both before and after the vacuum annealing are consistently higher than those of Ni-P of the same thickness. Consequently, the sharp increase in resistivity for thinner films sets in at a larger thickness for Ni-B.

The initial state of Ni-B is a solid solution of boron in nickel. It seems likely that the internal structure of Ni-B islands shows the separation of nickel-rich regions from boron-rich regions. Thus the conduction electrons have to pass through a poorly conducting material in going from one island to another island to another island. This conjecture is strengthened by the experimental result that the sharp rise in resistivity for discontinuous films occurs at a larger
thickness for Ni-B than Ni-P.

5.2 Future Work

Electrolessly deposited Ni-P (pH = 5.3) films have been studied extensively for many years. In contrast, little work on electroless Ni-B thin films has been reported. Our work on the structural and electrical properties of electroless Ni-B is only a start.

The growth mechanism, the optical, mechanical, and magnetic properties are all interesting subjects for future work. It would also be of interest to extend the present work to films deposited using the catalytic pretreatment system.
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