1992

Morphological studies of quasi amorphous systems using atomic radial distribution functions.

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**MORPHOLOGICAL STUDIES
OF
QUASI AMORPHOUS SYSTEMS
USING
ATOMIC RADIAL DISTRIBUTION FUNCTIONS**

**by
Danko Simunovich**

**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
1992**

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ISBN 0-315-78877-1

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ABSTRACT

Electron diffraction patterns from thin films of electroless nickel and copper, electroplated copper and a two layer system consisting of electroplated copper upon electroless nickel, are analyzed in terms of reduced radial distribution functions (reduced RDF) of the atoms. Computing theoretical reduced RDF and comparing them to the experimental ones, proves to be a practical means for determining the degree of crystallinity along with any strain (or lattice distortions) that may be present in a quasi amorphous lattice.

ACKNOWLEDGEMENT

I would like to express my appreciation to Dr. M. Schlesinger for his continued interest and advice throughout this work. I would also like to express my gratitude to Mr. S. Gillen for the timed A-D converter interface and to Mr. J. Robinson for taking the electron diffraction patterns. Most of all, I would like to thank my parents for their support and love.

TABLE OF CONTENTS

ABSTRACT	iv
ACKNOWLEDGEMENT	v
INTRODUCTION	vii
CHAPTER I	THEORETICAL CONSIDERATIONS
1. Calculation of Elastic Scattering by the Born Approximation	1
2. Scattering by a Small Crystal	6
3. Scattering by Quasi Amorphous Systems	12
4. Scaling and Normalization of the Scattered Electron Intensity Curves	18
5. Radial Distribution Functions	21
CHAPTER II	EXPERIMENTAL
6. Preparation of Films	33
7. Electron Diffraction Patterns	36
8. Determination of Crystallite Sizes and the Presence of Strain	37
CHAPTER III	EXPERIMENTAL RESULTS
9. Ni-P Films	38
10. Cu Films	52
11. Ni-Cu Film	62
CHAPTER IV	CONCLUSION
REFERENCES	69
VITA	71

INTRODUCTION

Structural studies of electroless thin Ni-P and Cu films have been conducted in the past^(1,2). In these studies, arguments have been made about the degree of local order by analyzing their electron diffraction patterns in terms of reduced radial distribution functions (reduced RDF) of the atoms. The present study applies reduced RDF techniques to these same systems as well as to theoretical electron beam diffraction intensity curves from fcc crystallites, in order to demonstrate a practical method of determining crystallite sizes as well as any strain (or lattice distortions). The comparison of experimental reduced RDF curves to theoretically calculated ones is essential when examining for strain (or lattice distortions), as the peaks in these curves are broadened to a degree due to termination of data at finite scattering vectors.

Thin films in this study are a few hundred Angstroms in thickness. They possess an extremely large surface to volume ratio. The material density for such thin films is lower than that of bulk, which is associated with internal voids⁽³⁾. This all contributes to the notion that the atoms in these films exist in a different environment from that of bulk, i.e. interatomic distances within individual crystallites may differ from that of bulk and stress may be too a factor.

The utility of the reduced RDF technique can also be evident

in studying a thin film consisting of alternating layers of epitaxially grown materials A and B. Such layers can be created by, vacuum evaporation of one thin metal layer upon another, alternate electrodeposition or electroless deposition of thin layers using two different electrolytes, or various combinations of these methods. Koehler⁽⁴⁾ proposed some basic criteria for the selection of the metals A and B. He suggested that the two metals have nearly equal lattice parameters and thermal coefficients of expansion to minimize interfacial strains, as well as strong bond strengths between layers. A thin film consisting of alternating layers of nickel and copper fits such criteria and is of industrial interest due to its high strength⁽⁵⁾.

In this work a study is conducted on a two layer system consisting of electroplated copper upon electroless nickel. The atomic percentage of nickel and copper in this film is approximately the same and the entire film is not more than a few hundred Angstroms thick. As such, the film can be considered as an interface and the reduced RDF technique is applied in order to reveal the atomic features.

This thesis is divided into four chapters. Chapter I is an overview of electron scattering theory leading up to the development of the reduced RDF. Chapter II deals with the experimental procedures. Chapter III presents the experimental results and chapter IV gives the conclusion.

CHAPTER I

THEORETICAL CONSIDERATIONS

1. Calculation of Elastic Scattering by the Born Approximation

In the case of elastic scattering of electrons by an atom, the quantum state of the atom is unchanged and therefore the internal structure of the atom can be disregarded. The interaction of the atom with the incident electrons may then be considered as equivalent to that of a centre of force. The Schrödinger equation for scattering of electrons by a potential $V(\mathbf{r})$ becomes

$$\nabla^2 \psi + k^2 \psi = 2 \frac{\pi}{\hbar^2} V(\mathbf{r}) \psi, \quad [1]$$

with boundary conditions that $\exp(i\mathbf{k} \cdot \mathbf{r})$ is the plane wave representing the flux of incident electrons and $f(\mathbf{k}, \mathbf{k}') e^{i\mathbf{k}' \cdot \mathbf{r}} / r$ is the outgoing wave representing scattered electrons at large r beyond the range of force. The spatial variation of the scattered wave is described by $e^{i\mathbf{k}' \cdot \mathbf{r}} / r$.

By superposition, the asymptotic solution to Eq. [1] becomes

$$\psi \sim \exp(i\mathbf{k} \cdot \mathbf{r}) + f(\mathbf{k}, \mathbf{k}') \frac{e^{i\mathbf{k}' \cdot \mathbf{r}}}{r}. \quad [2]$$

The vector $\mathbf{k}$ points in the direction of incidence and, the vector $\mathbf{k}'$ in that of $\mathbf{r}$ (direction of observation) with the condition

$$|\mathbf{k}| = |\mathbf{k}'| = 2mE/\hbar.$$

The use of a Green's function⁽⁶⁾ will enable us to convert partial differential equation [1] into an integral equation. In order to use this approach, consider separating the incident wave, $\exp(i\mathbf{k}\cdot\mathbf{r})$, from the wave function, and write

$$\psi = \exp(i\mathbf{k}\cdot\mathbf{r}) + \psi_s, \quad [3]$$

where ψ_s represents the flux of scattered electrons.

Since $\exp(i\mathbf{k}\cdot\mathbf{r})$ is a particular solution of the homogeneous wave equation, i.e.

$$(\nabla^2 + k^2) \exp(i\mathbf{k}\cdot\mathbf{r}) = 0, \quad [4]$$

the Schrödinger equation [1] now becomes

$$(\nabla^2 + k^2) \psi_s = f(\mathbf{r}) \quad [5]$$

where $f(\mathbf{r}) = 2mV(\mathbf{r})\psi/\hbar^2$.

The Green's function is defined as the solution of the problem for a point "source" $f(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}')$ of unit intensity so that if the solution of

$$(\nabla^2 + k^2) G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \quad [6]$$

is known, then the solution of Eq. [5] is

$$\psi_s = \int G(\mathbf{r}, \mathbf{r}') f(\mathbf{r}') d\mathbf{r}'. \quad [7]$$

The Green's function satisfying equation [6] and having the proper asymptotic form is given by⁽⁷⁾

$$G(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \frac{\exp(ik|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|}. \quad [8]$$

On substituting for $G(\mathbf{r}, \mathbf{r}')$ and $f(\mathbf{r}')$ in Eq. [7], the electron wave function, Eq. [3], becomes

$$\psi(\mathbf{r}) = \exp(i\mathbf{k} \cdot \mathbf{r}) - \frac{1}{4\pi} \cdot \frac{2m}{\hbar^2} \int \frac{\exp(ik|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}'. \quad [9]$$

The method of successive approximations may be applied to Eq. [9] to develop the Neumann series for the solution.⁽⁸⁾ The first approximation $\psi(\mathbf{r}) \approx \exp(i\mathbf{k} \cdot \mathbf{r})$ is substituted into Eq. [9] under the integral sign to obtain a second approximation. The process is then iterated giving the Neumann series

$$\begin{aligned} \psi(\mathbf{r}) = & \exp(i\mathbf{k} \cdot \mathbf{r}) - \frac{1}{4\pi} \cdot \frac{2m}{\hbar^2} \int G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \exp(i\mathbf{k} \cdot \mathbf{r}') d\mathbf{r}' \\ & + \left(-\frac{1}{4\pi} \cdot \frac{2m}{\hbar^2}\right)^2 \iint G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') G(\mathbf{r}', \mathbf{r}'') V(\mathbf{r}'') \exp(i\mathbf{k} \cdot \mathbf{r}'') d\mathbf{r}'' d\mathbf{r}' + \dots \quad [10] \end{aligned}$$

Keeping only the first iteration gives

$$\psi(\mathbf{r}) \approx \exp(i\mathbf{k} \cdot \mathbf{r}) - \frac{1}{4\pi} \cdot \frac{2m}{\hbar^2} \int \frac{\exp(ik|\mathbf{r} - \mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} V(\mathbf{r}') \exp(i\mathbf{k} \cdot \mathbf{r}') d\mathbf{r}' \quad [11]$$

which is referred to as the first Born approximation.

When the intensity of the scattered wave $|\psi_s(\mathbf{r})|^2$, near the scattering centre is small compared to the intensity of the incident wave $|\psi_i(\mathbf{r})|^2$, the Born approximation is valid⁽⁹⁾. From Eq. [11], the ratio of $|\psi_s(\mathbf{r})|^2$ to $|\psi_i(\mathbf{r})|^2$ at the centre of an atom having a spherically symmetric field $V(r)$ is

$$\frac{|\psi_s(0)|}{|\psi_i(0)|} = \frac{1}{4\pi} \cdot \frac{2m}{\hbar^2} \left| \int_0^{2\pi} d\phi' \int_0^\pi e^{ikr' \cos \theta'} \sin \theta' d\theta' \int_0^\infty V(r') e^{ikr' r'} dr' \right|, \quad [12]$$

where $\mathbf{k}$ has been taken parallel to the polar axis $\theta=0$. With the change of variable $\xi' = \cos \theta'$, and after a simple integration over ξ'

and ϕ' , we find

$$\frac{|\psi_s(0)|}{|\psi_i(0)|} = \frac{2m}{\hbar^2} \left| \int_0^\infty V(r') \frac{\sin kr'}{kr'} e^{ikr'r'} dr' \right|. \quad [13]$$

Eq. [13] shows that as the electron energy becomes large (k large), the integral becomes smaller and the Born approximation is valid.

Consider now the asymptotic form of the scattered wave $\psi_s(r)$. From the triangle shown in figure. 1, we have

$$|\mathbf{r}-\mathbf{r}'| = [r^2 - 2\mathbf{r}\cdot\mathbf{r}' + r'^2]^{1/2} \quad [14]$$

If $\mathbf{r}$ is sufficiently distant so that $r'/r \ll 1$, we may expand Eq. [14] to obtain

$$|\mathbf{r}-\mathbf{r}'| \approx r \left[1 - \frac{2\mathbf{r}\cdot\mathbf{r}'}{r^2} \right]^{1/2} \approx r - \mathbf{r}'\cdot\hat{\mathbf{r}}. \quad [15]$$

Then the arguments of the exponential terms in the scattered wave $\psi_s(\mathbf{r})$ can be written as

$$\begin{aligned} & ikr - ikr'\cdot\hat{\mathbf{r}} + i\mathbf{k}\cdot\mathbf{r}' \\ & = ikr + 2\pi i \frac{(\hat{\mathbf{r}} - \hat{\mathbf{r}}')}{\lambda} \cdot \mathbf{r}' \\ & = ikr + 2\pi i \mathbf{s} \cdot \mathbf{r}', \end{aligned} \quad [16]$$

from which we defined $\mathbf{s}$ as

$$\mathbf{s} = \frac{(\hat{\mathbf{r}} - \hat{\mathbf{r}}')}{\lambda} = \frac{(\mathbf{k} - \mathbf{k}')}{2\pi} \quad [17]$$

with

$$|\mathbf{s}| = \frac{2\sin\theta}{\lambda} \quad [18]$$

termed the scattering vector, and 2θ is the scattering angle.

Figure 1. Illustrates the choice of vectors. The origin O is taken at the centre of the atom. A plane incident wave travelling in the $\hat{z}$ direction is scattered at all points $\mathbf{r}'$ within the sphere of interaction by $V(\mathbf{r}')$. The scattering contribution from all points $\mathbf{r}'$ is then summed to obtain the total wave at some observation point $\mathbf{r}$.

The asymptotic form of the scattered wave $\psi_s(\mathbf{r})$ becomes

$$\psi_s(\mathbf{r}) \sim -\frac{1}{4\pi} \cdot \frac{2m}{\hbar^2} \frac{e^{ikr}}{r} \int e^{2\pi i \mathbf{s} \cdot \mathbf{r}'} V(\mathbf{r}') d\mathbf{r}'. \quad [19]$$

Comparison of Eq. [19] with Eq. [2] shows that the amplitude of the scattered wave is

$$f(\mathbf{s}) = -\frac{1}{4\pi} \cdot \frac{2m}{\hbar^2} \int e^{2\pi i \mathbf{s} \cdot \mathbf{r}} V(\mathbf{r}) d\mathbf{r}. \quad [20]$$

For a spherically symmetric potential, the angular part of the integration in Eq. [20] can be carried out. Using spherical polar coordinates with the axis parallel to $\mathbf{s}$ and integrating in a similar manner as Eq. [12], we obtain

$$f(s) = \frac{2me}{\hbar^2} \int_0^\infty \frac{\sin 2\pi s r}{2\pi s r} \varphi(r) r^2 dr \quad [21]$$

where $\varphi(r)$ is the effective atomic potential. The function $f(s)$ is referred to as the atomic scattering factor. In our calculations we have used the values of $f(s)$ as given by Doyle and Turner⁽¹⁰⁾.

2. Scattering by a Small Crystal

In section 1, we saw that if an electron wave is incident on an atom, the scattered amplitude at an angle 2θ from the direction of incidence is given by $f(s)$. Therefore, $f(s)$ for a particular atom is a measure of its scattering power. By simple geometric-optic arguments, we wish to calculate the scattered amplitude when an electron wave is incident on a small crystal. Referring to figure 2, an electron wave scattered from an atom at origin O , is perceived at a distant point $\mathbf{r}$ with a phase factor $e^{i\mathbf{k} \cdot \mathbf{r}}$. Therefore the wave function representing the scattered electron wave by an atom at origin O , for a unit incoming wave, at large $\mathbf{r}$ is

$$\psi_{s_o}(\mathbf{r}) = f_o(s) \frac{e^{i\mathbf{k} \cdot \mathbf{r}}}{r}, \quad [22]$$

where $f_o(s)$ is a measure of the scattering power of the atom at O .

All tables of $f(s)$ for electrons are based on calculations for free atoms. Here we neglect the effect on $f(s)$ due to neighbouring atoms.

Figure 2. Illustrating the choice of vectors, in order to express the scattered electron wave at various points r_p , as seen at an observation point r , in terms of an arbitrary origin O .

An electron wave scattered from an atom at p starts out with the phase factor $\exp(ik \cdot r_p)$, so that the total phase factor in the direction of observation r is $\exp(ik \cdot r_p + ik|r - r_p|)$. Then the wave function representing the scattered electron wave by an atom at p , for a unit incoming wave, at large r is

$$\psi_{s_p}(r) = f_p(s) \frac{e^{ikr_p + ik|r-r_p|}}{|r-r_p|}, \quad [23]$$

where $f_p(s)$ is a measure of the scattering power of an atom at p .

Since $r_p/r \ll 1$, we may expand $|r - r_p|$ in the exponential term of Eq. [23] as was done in Eq. [15] to obtain

$$|r - r_p| = r - r_p \cdot \hat{r}. \quad [24]$$

The exponential term in Eq. [23] can now be written as

$$\begin{aligned} & ikr - ikr_p \cdot \hat{r} + ik r_p \cdot \hat{r} \\ & = ikr + i(k - k') \cdot r_p, \because k' = k\hat{r} \\ & = ikr + 2\pi i s \cdot r_p \end{aligned} \quad [25]$$

where s is the scattering vector given in Eq. [17]. Then Eq. [23] for the scattered wave at large r by an atom at point p shown in figure 2, can now be written as

$$\psi_{s_p}(r) = f_p(s) \frac{e^{ikr}}{r} \cdot e^{2\pi i s \cdot r_p}. \quad [26]$$

The amplitude is seen to depend on the phase factor $\exp(2\pi i s \cdot r_p)$. Now consider the total amplitude scattered by an array of N atoms located at positions $r_1, r_2, \dots, r_N$, relative to some origin and having scattering factors $f_1(s), f_2(s), \dots, f_N(s)$. The total amplitude of the scattered wave in a direction parallel to $k' / |k|$ becomes

$$A(s) = \sum_{p=1}^N f_p(s) e^{2\pi i s \cdot r_p}. \quad [27]$$

Taking the square of the wave amplitude in Eq. [27], the intensity of the scattered wave becomes

$$I(\mathbf{s}) = \sum_{p=1}^N f_p(\mathbf{s}) e^{2\pi i \mathbf{s} \cdot \mathbf{r}_p} \sum_{q=1}^N f_q(\mathbf{s}) e^{-2\pi i \mathbf{s} \cdot \mathbf{r}_q}, \quad [28]$$

where we have now introduced a second set of vectors $\mathbf{r}_q$ which run over the same atomic positions as $\mathbf{r}_p$. Now consider decomposing these vectors into a vector $\mathbf{p}$ which locates all the unit cells within a crystal and a vector $\mathbf{r}_j$ which locates all atoms within the unit cell. Assume that the crystal has the shape of a parallelepiped containing $N_1 N_2 N_3$ cells, with edges $N_1 \mathbf{a}, N_2 \mathbf{b}, N_3 \mathbf{c}$ parallel to the axes $\mathbf{a}, \mathbf{b}$, and $\mathbf{c}$. Now the position of any atom of type j , in a unit cell lmn is given by

$$\mathbf{p} + \mathbf{r}_j = l\mathbf{a} + m\mathbf{b} + n\mathbf{c} + \mathbf{r}_j \quad [29]$$

On inserting Eq. [29] in Eq. [28], we obtain

$$I(\mathbf{s}) = |F|^2 \left| \sum_{l=0}^{N_1-1} e^{2\pi i l \mathbf{s} \cdot \mathbf{a}} \right|^2 \left| \sum_{m=0}^{N_2-1} e^{2\pi i m \mathbf{s} \cdot \mathbf{b}} \right|^2 \left| \sum_{n=0}^{N_3-1} e^{2\pi i n \mathbf{s} \cdot \mathbf{c}} \right|^2 \quad [30]$$

where

$$F(\mathbf{s}) = \sum_j f_j(\mathbf{s}) e^{2\pi i \mathbf{s} \cdot \mathbf{r}_j} \quad [31]$$

is called the geometrical structure factor⁽¹¹⁾ as it involves the coordinates of the atoms in the unit cell.

Using the series identities

$$\sum_{l=0}^{N_1-1} x^l = \sum_{l=0}^{\infty} x^l - \sum_{l=N_1}^{\infty} x^l = \frac{1}{1-x} - \frac{x^{N_1}}{1-x} \quad [32]$$

with $x = e^{2\pi i s \cdot a}$, we obtain in general

$$\left| \sum_{l=0}^{N_1-1} e^{2\pi i l s \cdot a} \right|^2 = \frac{\sin^2 N_1 (\pi s \cdot a)}{\sin^2 (\pi s \cdot a)}. \quad [33]$$

The intensity of the scattered wave, Eq. [30], can now be written as

$$I(s) = |F|^2 \frac{\sin^2 N_1 (\pi s \cdot a)}{\sin^2 (\pi s \cdot a)} \cdot \frac{\sin^2 N_2 (\pi s \cdot b)}{\sin^2 (\pi s \cdot b)} \cdot \frac{\sin^2 N_3 (\pi s \cdot c)}{\sin^2 (\pi s \cdot c)}. \quad [34]$$

The function $\sin^2 Nx / \sin^2 x$ rises to maxima N^2 at values of x which are integral multiples of π . Therefore, for $I(s)$ to be a maximum, we must simultaneously satisfy the three conditions

$$\begin{aligned} s \cdot a &= h \\ s \cdot b &= k \\ s \cdot c &= l \end{aligned} \quad [35]$$

where the quantities (hkl) are the three Miller indices which are used in the representation of crystallographic planes. These three equations are known as the Laue equations and they can be simultaneously satisfied only if s , the scattering vector, is a reciprocal lattice vector given by

$$s = hA + kB + lC \quad [36]$$

where

$$A = \frac{b \times c}{a \cdot (b \times c)}; \quad B = \frac{c \times a}{a \cdot (b \times c)}; \quad C = \frac{a \times b}{a \cdot (b \times c)}. \quad [37]$$

Now consider a set of parallel equidistant planes (hkl) , one of which passes through the origin, and the other intercepting the

three crystallographic axes a, b, c at $a/h, b/k, c/l$. This is illustrated in figure 3. From the figure, $(a/h - b/k)$ and $(c/l - a/h)$ are vectors which are parallel to the (hkl) planes. With the use of the fundamental vectors of the reciprocal lattice given by Eq. [37], we have

$$\begin{aligned} \left(\frac{a}{h} - \frac{b}{k}\right) \cdot \mathbf{s} &= \left(\frac{a}{h} - \frac{b}{k}\right) \cdot (h\mathbf{A} + k\mathbf{B} + l\mathbf{C}) = 0, \\ \left(\frac{c}{l} - \frac{a}{h}\right) \cdot \mathbf{s} &= \left(\frac{c}{l} - \frac{a}{h}\right) \cdot (h\mathbf{A} + k\mathbf{B} + l\mathbf{C}) = 0. \end{aligned} \quad [38]$$

Figure 3. Representation of the Crystallographic Planes (hkl) .

Therefore the scattering vector $\mathbf{s}$ is perpendicular to the set of (hkl) planes, since it is perpendicular to two vectors which are

parallel to the planes.

Now let d_{hkl} be the perpendicular distance between planes and $\hat{n}$ a unit vector parallel to the scattering vector $\mathbf{s}$ and as follows from the above discussion also perpendicular to the (hkl) planes. Then we see that

$$d_{hkl} = \frac{\mathbf{a}}{h} \cdot \hat{n} = \frac{\mathbf{a}}{h} \cdot \frac{\mathbf{s}}{|\mathbf{s}|} = \frac{\mathbf{a} \cdot (h\mathbf{A} + k\mathbf{B} + l\mathbf{C})}{h|\mathbf{s}|} = \frac{1}{|\mathbf{s}|}. \quad [39]$$

Therefore the spacing d_{hkl} of the planes (hkl) of the crystal lattice is equal to $1/|\mathbf{s}|$. Substituting Eq. [18] into Eq. [39], we obtain

$$2d_{hkl}\sin\theta = \lambda, \quad [40]$$

which is Bragg's law.

3. Scattering by Quasi Amorphous Systems

In the previous section we dealt with the scattering from a small crystal where the atoms are arranged in a periodic manner with their position vectors given by Eq. [29]. Then the summation in Eq. [28] for the scattered intensity formed a geometric progression which could be evaluated. If we are dealing with quasi amorphous systems such as electrolessly deposited thin metal films possessing only local atomic order, no simple relationship exists between the position vectors.

Introducing the difference vector $\mathbf{r}_{pq} = \mathbf{r}_p - \mathbf{r}_q$, Eq. [28] for the scattered intensity becomes

$$I(\mathbf{s}) = \sum_{p=1}^N \sum_{q=1}^N f_p(\mathbf{s}) f_q(\mathbf{s}) e^{2\pi i \mathbf{s} \cdot \mathbf{r}_{pq}} \quad [41]$$

Because only local atomic order exists in quasi amorphous materials and individual crystallites are randomly oriented, such materials can be considered as being isotropic. As such, there is justification in assuming that the individual crystallites assume with equal probability all orientations in space relative to $\mathbf{s}$. Taking the angle between $\mathbf{s}$ and $\mathbf{r}_{pq}$ to be α , the average for each exponential term in Eq. [41] is given by

$$\langle e^{2\pi i \mathbf{s} \cdot \mathbf{r}_{pq}} \rangle = \frac{1}{4\pi r_{pq}^2} \int_0^\pi e^{2\pi i s r_{pq} \cos \alpha} 2\pi r_{pq}^2 \sin \alpha d\alpha = \frac{\sin 2\pi s r_{pq}}{2\pi s r_{pq}}. \quad [42]$$

Substituting this result in Eq. [41], we obtain for the average elastic scattered intensity

$$I(\mathbf{s}) = \sum_{p=1}^N \sum_{q=1}^N f_p(\mathbf{s}) f_q(\mathbf{s}) \frac{\sin 2\pi s r_{pq}}{2\pi s r_{pq}}, \quad [43]$$

which is known as the Debye scattering equation. This equation can be split into two parts - one in which the $p=q$ and the other for which $p \neq q$. We then obtain

$$I(\mathbf{s}) = \sum_{j=1}^N f_j^2(\mathbf{s}) + \sum_{p=1}^N \sum_{q \neq p}^N f_p(\mathbf{s}) f_q(\mathbf{s}) \frac{\sin 2\pi s r_{pq}}{2\pi s r_{pq}}. \quad [44]$$

The scattered beams which fall on a photographic emulsion produce circular diffraction patterns. This is because the crystallites in the sample are randomly oriented, and as a result the beam scattered from each crystallite at an angle 2θ from the

incident beam will be in a different direction. Therefore the sum of all these scattered beams for a particular angle 2θ produce a cone of radiation. We see that the averaging of the exponential term in Eq. [41], is equivalent to stating that the scanning of the intensity may be performed along any radius of the diffraction rings.

The full width at half maximum peak intensity for each cone is dictated by Eq. [44]. For a particular scattering vector s , the terms in the double sum of Eq. [44] will add destructively or constructively to the intensity depending on the geometry of the crystallite. If the terms in the double sum add constructively, we have an allowed diffraction line corresponding to a particular (hkl) plane. The broadening for these allowed lines will decrease as the terms in the double sum increase. Since the number of atoms in each of the crystallites is a few hundred or less, these lines are very broad. We will now illustrate this for a one component system containing crystallites with a face-centered cubic space lattice which has the rhombohedral primitive cell shown in figure 4. Neglecting intercrystallite interferences, we can obtain the average scattered intensity for this system by evaluating Eq. [44] for an N atom crystallite. The primitive translation vectors are

$$\mathbf{a}' = \frac{a}{2} (\hat{x} + \hat{y}); \quad \mathbf{b}' = \frac{a}{2} (\hat{y} + \hat{z}); \quad \mathbf{c}' = \frac{a}{2} (\hat{z} + \hat{x}); \quad [45]$$

where a is the lattice constant. Using the primitive translation vectors as a basis, the radial distance of any atom p from q in our face-centered cubic crystallite is given by

$$r_{pq} = \frac{a}{2} \sqrt{(p_1 + p_3 - q_1 - q_3)^2 + (p_1 + p_2 - q_1 - q_2)^2 + (p_2 + p_3 - q_2 - q_3)^2}, \quad [46]$$

where the p's and q's are arbitrary integers. The scattered intensity given by Eq. [44] is calculated for a Ni crystallite containing 125 atoms and one containing 343 atoms, shown in figure 5. The distinguishing features between the two curves are, the full width at half maximum peak intensity for each line and the development of the scattered intensity from the (200) plane as the crystallite size is increased.

Figure 4. The primitive basis vectors of the face-centered cubic lattice.

Figure 5. The broadening of the scattered intensities for a Ni crystallite as it is increased from 125 atoms to 343 atoms.

4. Scaling and Formalization of the Scattered Electron Intensity Curves

Consider electrons scattered at an angle 2θ from the direction of incidence to form a cone of radiation of radius R on a photographic emulsion. If the distance from the specimen plane to the photographic plane is L , we can write

$$2\theta = \frac{R}{L} \quad [47]$$

for scattering at small angles. The distance L is really an effective distance, since the lens systems (intermediate and projector lenses) focus and expand the electron beam. Combining this with the Bragg condition given by Eq. [40], we obtain

$$R = \frac{\lambda L}{d_{hkl}} = \lambda L |s|, \quad [48]$$

which shows that the radii of the diffraction rings are proportional to the scattering vector s . The constant of proportionality, λL , is called the camera constant and it must be determined for a fixed operating condition of the electron microscope in order to scale the horizontal axis for the scattered electron intensity curves.

Using the definition for the reciprocal lattice vectors, Eq. [37], the scattering vector s for a cubic space lattice becomes

$$|s| = \frac{1}{d_{hkl}} = [(hA + kB + lC) \cdot (hA + kB + lC)]^{1/2} = \frac{(h^2 + k^2 + l^2)^{1/2}}{a}, \quad [49]$$

where a is the lattice parameter. Combining this with Eq. [48], we can write

$$(h^2+k^2+l^2)^{1/2} = \frac{a}{\lambda L} R. \quad [50]$$

Using the diffraction pattern of a known standard, Eq. [50] can be plotted in the form of a straight line with slope $a/\lambda L$, from which the camera constant can be obtained. The horizontal axis of the scattered beam intensity curve for any unknown material can then be scaled.

In the next section, we shall see that we can write the scattered electron intensity as

$$I(s) = N \sum_{j=1}^n x_j f_j^2(s) + N \sum_{i=1}^n \sum_{j=1}^n x_i f_i(s) f_j(s) \int_0^\infty 4\pi r^2 [\rho_{ij}(r) - \bar{\rho}_{ij}] \frac{\sin 2\pi sr}{2\pi sr} dr. \quad [51]$$

Here x_j is the atomic fraction of atoms having scattering factor $f_j(s)$, $\rho_{ij}(r)$ the average density of j -type atoms in spherical shells of radius r about i -type atoms and $\bar{\rho}_{ij}$ the constant mean density of j -type atoms. An examination of this equation indicates that $I(s)/N$ oscillates about $\sum_{j=1}^n x_j f_j^2(s)$ for large values of the scattering vector s . This is illustrated for the one component case by superimposing the square of the atomic scattering factor ($f^2(s)$) on a calculated scattered intensity curve (using Debye Eq. [44]) for a 343 Ni atom crystallite (shown in figure 6). Therefore an experimental scattered intensity scale which is in arbitrary units can be normalized to $I(s)/N$ by multiplying it by a suitable factor so that it oscillates about $\sum_{j=1}^n x_j f_j^2(s)$ for large values of the scattering vector s .

Figure 6. $I(s)/N$ (calculated for a 343 Ni atom crystallite) oscillating about the square of the atomic scattering factor ($f^2(s)$).

5. Radial Distribution Functions

In this section, we develop a method to analyze the scattered electron intensity from a quasi amorphous system in terms of reduced radial distribution functions (reduced RDF) of the atoms. Detailed information on RDF is given by Warren⁽¹²⁾ and Dove⁽¹³⁾, and we will primarily follow the treatment of Dove here.

Consider the scattered electron intensity from a quasi amorphous system given by Eq. [44]. By introducing $\rho_{ij}(r)$ as the average atomic density of j-type atoms in spherical shells of radius r about i-type atoms, the summation may be replaced by integration over the sample volume. Here spherical symmetry exists because individual crystallites in the sample are assuming all orientations with equal probability. Now let $x_1, x_2, \dots, x_n$ be the atomic fraction of atoms with scattering factors $f_1, f_2, \dots, f_n$, then Eq. [44] becomes

$$I(s) = N \sum_{j=1}^n x_j f_j^2(s) + N \sum_{i=1}^n \sum_{j=1}^n x_i f_i(s) f_j(s) \int 4\pi r^2 \rho_{ij}(r) \frac{\sin 2\pi sr}{2\pi sr} dr \quad [52]$$

Letting $\bar{\rho}_{ij}$ be the constant mean density of j-type atoms and making the substitution $\rho_{ij}(r) = \bar{\rho}_{ij} + \bar{\rho}_{ij}$ for $\rho_{ij}(r)$, we obtain

$$\begin{aligned} I(s) = & N \sum_{j=1}^n x_j f_j^2(s) \\ & + N \sum_{i=1}^n \sum_{j=1}^n x_i f_i(s) f_j(s) \int 4\pi r^2 [\rho_{ij}(r) - \bar{\rho}_{ij}] \frac{\sin 2\pi sr}{2\pi sr} dr \quad [53] \\ & + N \sum_{i=1}^n \sum_{j=1}^n x_i f_i(s) f_j(s) \int 4\pi r^2 \bar{\rho}_{ij} \frac{\sin 2\pi sr}{2\pi sr} dr. \end{aligned}$$

The third term in Eq. [53] corresponds to scattering at such

extremely small angles that it is hidden by the primary beam and therefore unobservable⁽¹²⁾. Neglecting it, Eq. [53] becomes

$$I(s) = N \sum_{j=1}^n x_j f_j^2(s) + N \sum_{i=1}^n \sum_{j=1}^n x_i f_i(s) f_j(s) \int_0^{\infty} 4\pi r^2 [\rho_{ij}(r) - \bar{\rho}_{ij}] \frac{\sin 2\pi sr}{2\pi sr} dr. \quad [54]$$

Here the integration is taken from zero to infinity, since $[\bar{\rho}_{ij}(r) - \rho_{ij}]$ goes to zero at large r as a result of finite crystallite sizes.

Defining

$$i(s) = s \left[\frac{I(s)}{N} - \sum_{j=1}^n x_j f_j^2(s) \right] / \langle f(s) \rangle^2, \quad [55]$$

where

$$\langle f(s) \rangle^2 = \sum_{i=1}^n x_i f_i(s) \sum_{j=1}^n x_j f_j(s), \quad [56]$$

we obtain from Eq. [54],

$$4\pi i(s) = \sum_{i=1}^n \sum_{j=1}^n x_i \frac{f_i(s) f_j(s)}{\langle f(s) \rangle^2} \int_0^{\infty} 4\pi r [\rho_{ij}(r) - \bar{\rho}_{ij}] \sin 2\pi sr dr. \quad [57]$$

The quantity $i(s)$ is derived from diffraction data and is often called the reduced scattered intensity.

Taking the Fourier transform ($\mathcal{F}$) with respect to s of both sides of Eq. [57], we obtain

$$4\pi \mathcal{F}\{i(s)\} = \sum_{i=1}^n \sum_{j=1}^n x_i \mathcal{F}\left\{\frac{f_i(s) f_j(s)}{\langle f(s) \rangle^2}\right\} * \mathcal{F}\left(\int_{-\infty}^{\infty} 4\pi r [\rho_{ij}(r) - \bar{\rho}_{ij}] \sin 2\pi s r dr\right), \quad [58]$$

where the asterisk (*) denotes convolution, i.e. here we have used the convolution theorem which states, that the Fourier transform of the product of two functions is equal to the convolution product of the transforms of the functions. Letting the two functions be $h(s)$ and $x(s)$ with $\mathcal{F}\{h(s)\} = H(r)$ and $\mathcal{F}\{x(s)\} = X(r)$, we can write the convolution theorem symbolically as

$$\mathcal{F}\{h(s) x(s)\} = \mathcal{F}\{h(s)\} * \mathcal{F}\{x(s)\} = H(r) * X(r) = \int_{-\infty}^{\infty} H(\tau) X(r-\tau) d\tau. \quad [59]$$

Denoting $\mathcal{F}^{-1}$ as the inverse Fourier transform, by definition we can write

$$\mathcal{F}^{-1}(4\pi r [\rho_{ij}(r) - \bar{\rho}_{ij}]) = \int_{-\infty}^{\infty} 4\pi r [\rho_{ij}(r) - \bar{\rho}_{ij}] \sin 2\pi s r dr, \quad [60]$$

so that Eq. [58] becomes

$$4\pi \int_{-\infty}^{\infty} i(s) \sin 2\pi s r ds = \sum_{i=1}^n \sum_{j=1}^n x_i \int_{-\infty}^{\infty} \frac{f_i(s) f_j(s)}{\langle f(s) \rangle^2} \cos 2\pi s r ds * 4\pi r [\rho_{ij}(r) - \bar{\rho}_{ij}]. \quad [61]$$

By defining the functions,

$$Q_{ij}(r) \equiv \int_{-\infty}^{\infty} \frac{f_i(s) f_j(s)}{\langle f(s) \rangle^2} \cos 2\pi s r ds \quad [62]$$

and

$$G_{ij}(r) \equiv 4\pi r [\rho_{ij}(r) - \bar{\rho}_{ij}], \quad [63]$$

Eq. [61] can be written as

$$4\pi \int_{-\infty}^{\infty} i(s) \sin 2\pi s r ds = \sum_{i=1}^n \sum_{j=1}^n x_i \int_{-\infty}^{\infty} Q_{ij}(\tau) G_{ij}(r-\tau) d\tau. \quad [64]$$

Eq. [64] indicates that the transform of $i(s)$ (derived from diffraction data) consists of functions $G_{ij}(r)$ known as the reduced radial distribution functions, convoluted with the functions $Q_{ij}(r)$ which depend on the atomic scattering factors. In the case of a two component system containing scattering factors which closely resemble each other, we can make an approximation in Eq. [64] by assuming the same angular dependence for the atomic scattering factors. Then $\mathcal{F}\{f_i(s)f_j(s)/\langle f(s) \rangle^2\} = \mathcal{F}\{1\} = \delta(r)$, and Eq. [64] becomes

$$\begin{aligned} 4\pi \int_{-\infty}^{\infty} i(s) \sin 2\pi s r ds &= \sum_{i=1}^n \sum_{j=1}^n x_i \int_{-\infty}^{\infty} \delta(\tau) G_{ij}(r-\tau) d\tau \\ &= \sum_{i=1}^n \sum_{j=1}^n x_i G_{ij}(r) \\ &= \sum_{i=1}^n \sum_{j=1}^n x_i 4\pi r [\rho_{ij}(r) - \bar{\rho}_{ij}]. \end{aligned} \quad [65]$$

We now see that the Fourier transform of $i(s)$ (Eq. 65) describes real-space structure, i.e. $G_{ij}(r)$. This is valid for heavy atoms whose atomic numbers differ from each other by one, for then their "scattering powers" will be very similar, especially at larger scattering vectors.

For the two component system, Ni-Cu, which is studied in this thesis, we assume the same angular dependence for the atomic scattering factors $f_{Ni}(s)$ and $f_{Cu}(s)$ (shown in figure 7).

Figure 7. The atomic scattering factors for nickel and copper as a function of the scattering vector s .

The validity for this approximation comes about by first computing the Fourier transform of $i(s)$ assuming that copper has the same atomic scattering factor as nickel and vice versa, and then noting no change in the positions of the interatomic distances. Hence, the convolution in Eq. [64] does not influence the positions of the interatomic distances in Ni-Cu, and the Fourier transform of $i(s)$ can be approximated by Eq. [65].

For the one component case, the Fourier transform of $i(s)$ is exactly given by

$$4\pi \int_{-\infty}^{\infty} i(s) \sin 2\pi s r ds = 4\pi r [\rho(r) - \rho_0] = G(r), \quad [66]$$

and is called the reduced radial distribution function denoted by $G(r)$. Here ρ_0 is the average macroscopic density.

In practice, the continuous Fourier transform of Eq. [66] is replaced by the discrete Fourier transform. Many aspects of the discrete Fourier transform, as well as an algorithm known as the Fast Fourier Transform (FFT) which efficiently computes discrete transforms, are described in a book by Brigham⁽¹⁴⁾. This FFT algorithm was used to compute the reduced RDF presented in this thesis.

To obtain the reduced radial distribution function $G(r)$, the reduced scattered intensity, $i(s)$, has to be determined ideally for an infinite range of the scattering vector s . Because the intensity falls off rapidly with increasing scattering vector, this is not possible even for electron beam energies of 100 keV with a wavelength $\lambda = 0.037 \text{ \AA}$. As a result the integration in Eq. [66] is

carried out up to a finite limit equal to $s_{\max}$ where the scattered electron intensity is no longer measurable. This is equivalent to multiplying the function $i(s)$ by the square wave truncation function given by

$$\begin{aligned} h(s) &= 1, |s| \leq s_{\max} \\ &= 0, |s| > s_{\max} \end{aligned} \quad [67]$$

which is shown in Fig. 8.

Truncation of $i(s)$ at $s_{\max}$ when it has not converged introduces rippling in $G(r)$. To see this, we have to consider the Fourier transform of $i(s)h(s)$ given by

$$\begin{aligned} 4\pi \int_{-\infty}^{\infty} i(s) h(s) \sin 2\pi s r ds &= 4\pi \mathcal{F}\{h(s)\} * \mathcal{F}\{i(s)\} \\ &= 8\pi s_{\max} \frac{\sin 2\pi s_{\max} r}{2\pi s_{\max} r} * r[\rho(r) - \rho_0] \quad [68] \\ &= 8\pi s_{\max} \int_{-\infty}^{\infty} \frac{\sin 2\pi s_{\max} \tau}{2\pi s_{\max} \tau} (r-\tau) [\rho(r-\tau) - \rho_0] d\tau. \end{aligned}$$

The Fourier transform of the square wave truncation function is shown in Fig. 9. It is seen to have large side-lobes and the convolution in Eq. [68] will therefore produce rippling in $G(r)$. The second feature is that the full width at half maximum of the main peak is 0.402 and the resulting reduced radial distribution function will be broadened with respect to the desired one. Because these side-lobes will produce false correlations in the function $G(r)$, we employ the Hanning function as a truncation function given by

$$h(s) = \frac{1}{2} + \frac{1}{2} \cos\left(\frac{\pi s}{s_{\max}}\right), \quad |s| \leq s_{\max} \quad [69]$$

$$= 0, \quad |s| > s_{\max}$$

which is shown in Fig. 10. The Fourier transform of this function is shown in Fig. 11 which exhibits low side-lobe characteristics. The full width at half maximum is 0.666 which is an acceptable compromise.

Figure 8. The square wave truncation function.

Figure 9. Fourier transform of the square wave truncation function.

Figure 10. The Hanning truncation function.

Figure 11. Fourier transform of the Hanning truncation function.

CHAPTER II

EXPERIMENTAL

6. Preparation of Films

Microscope slide glasses were coated with Formvar(4g polyvinylformal in 1 liter ethylene dichloride) and standard⁽¹⁵⁾ sensitizing (Sn II) and activating (Pd II) procedures followed prior to immersion in a electroless metallizing bath. So as to limit the number of changing parameters from system to system, all formvar substrates were identically prepared.

The compositions of the electroless Ni-P metallizing baths^(16,17) that were used in this study are given in Table 1 and Table 2. In what follows, these metallizing baths will be referred to as A and B respectively. The phosphorus content in these films was minimized to less than two atomic percent by increasing the pH (with the addition of sodium hydroxide) of metallizing bath A to 13.5 and that of metallizing bath B to 12.3 ⁽¹⁷⁾. This atomic percentage was determined using an electron microscope (JEOL Model JEM-100CX) equipped with an energy- dispersive x-ray spectral analysis attachment (Model 5400 made by Tracor Northern). This gives justification to treat these films as consisting exclusively of fcc nickel and that the scattered intensity contribution from tetragonal Ni₃P that may be present is entirely negligible.

Because quasi amorphous films are in a metastable state, a Ni-P sample whose metallizing bath is A, for comparison sake was heat treated for 6 hours at 300°C to increase the local crystallographic order ⁽¹⁸⁾.

The composition of the electroless Cu metallizing bath⁽¹⁹⁾ that was used in this study is given in Table 3. Because of the possibility of contaminants in the metallizing bath ending up in the copper lattice, a sample of electroplated Cu was investigated as well. It was plated on Formvar first made conductive by an extremely thin electroless layer of Cu.

Table 1. Composition of metallizing bath A.

(Nickel chloride) $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	7.5 g/liter
(Sodium hypophosphite) NaH_2PO_2	3.5 g/liter
(Citric acid) $\text{H}_3\text{C}_6\text{H}_5\text{O}_7\text{H}_2\text{O}$	19.8 g/liter
(Ammonium chloride) NH_4Cl	12.5 g/liter

Table 2. Composition of metallizing bath B.

(Nickel sulfate) $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	30 g/liter
(Sodium hypophosphite) NaH_2PO_2	10.6 g/liter
(Sodium citrate) $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$	100 g/liter
(Ammonium chloride) NH_4Cl	53.6 g/liter

Table 3. Composition of the Cu metallizing bath.

Solution A		Solution B	
(Copper Sulfate) CuSO ₄ · 5H ₂ O	8 g	(Paraformaldehyde) (CH ₂ O) _n	13 g
(Rochelle salt) NaKC ₄ H ₄ O ₆ · 4H ₂ O	20 g	(Sodium hydroxide) NaOH	8.6 g
(Sodium hydroxide) NaOH	5.6 g		
Distilled H ₂ O to make a 200 ml solution.		Distilled H ₂ O to make a 200 ml solution.	
Three parts A are added to one part B to make the electroless Cu metallizing bath.			

Also included in this study is a system composed of electroless Ni (using metallizing bath A) with Cu electroplated on top which will be referred to as a Ni-Cu sandwich. The Ni and Cu layers were deposited thick enough to be continuous. Therefore the physical nature of this two layer system is one which has distinct Ni and Cu regions in contact with each other. This system will be studied for the purpose of obtaining an understanding of the Ni-Cu interface. It should be noted that the thickness of this system is not more than a few hundred Angstroms, and as such, each atom within the sample "recognizes" the interface and thereby influenced by it. Energy-dispersive x-ray spectral analysis showed the content

in this film to be: 50.37 atomic % Ni, 47.06 atomic % Cu, and 2.57 atomic % P.

This represents six quasi amorphous systems whose scattered electron intensity will be analyzed in terms of radial distribution functions of the atoms (Ni-P films using metallizing baths A and B, heat treated Ni-P using metallizing bath A, electroless as well as electroplated Cu, and the Ni-Cu sandwich).

7. Electron Diffraction Patterns

Selected area diffraction (SAD) patterns were recorded photographically using an electron beam energy of 100 keV. The photographic films containing the SAD patterns were scanned by a densitometer interfaced to a 33 MHz 80386 PC.

Our SAD patterns contain a background component due to scattering from the sensitized and activated Formvar substrate. Consequently an intensity trace of a SAD pattern solely due to scattering from such a substrate was normalized with respect to "unwanted" peaks in the patterns from the six systems mentioned in the previous section, and then subtracted.

The horizontal axis for the scattered electron intensity curves were scaled using the diffraction pattern obtained from an Aluminum standard. Then the intensity scale which is in arbitrary units, was normalized to $I(s)/N$ by multiplying each of the curves by a suitable factor so that they oscillate about $f^2(s)$ (for the one component systems) and $x_{Ni}f^2_{Ni} + x_{Cu}f^2_{Cu}$ (for the Ni-Cu sandwich).

8. Determination of Crystallite Sizes and the Presence of Strain

The reduced radial distribution function, $G(r)$, gives the distances of neighboring atoms from a given origin atom. After a number of lattice parameters, the curve for $G(r)$ will "wash-out" as the density of atoms approaches the macroscopic mean density ρ_0 (see Eq. [66]). Suggestion pertaining to the size of our crystallites, can be obtained from the function $G(r)$ according to this "wash-out" region.

Knowledge of the crystallite sizes, will allow the computation of theoretical scattered intensity curves (using the Debye equation) and subsequent reduced RDF curves. Correlations between these calculated $G(r)$ curves and the experimental ones are then made in order to investigate the degree of strain (or any lattice distortions) that may be present. It should be noted, that it is imperative to compute the theoretical intensities up to an s value in accordance with the experimental curves, otherwise $G(r)$ will be altered and no meaningful correlations can be made.

The reason for not simply comparing experimental nearest etc. neighbor distances to that of actual bulk distances, is that the experimental $G(r)$ functions are broadened as a result of truncation of $i(s)$ (the reduced scattered intensity) when it has not converged. This broadening has been discussed in the section dealing with radial distribution functions.

CHAPTER III

EXPERIMENTAL RESULTS

9. Ni-P Films

Figure 12 shows the normalized scattered electron intensity curve for a Ni-P sample obtained using metallizing bath A. The corresponding reduced RDF curve, $G(r)$, is depicted in figure 13. This is to be compared to a theoretical scattered intensity curve and subsequent reduced RDF curve calculated for a Ni crystallite containing 343 atoms (shown in figures 14 and 15 respectively). This corresponds to a cubic crystallite with sides of approximately four lattice parameters in length.

Looking at the theoretical $G(r)$ curve (figure 15), "washing-out" starts to occur after the eighth peak which is located at a distance of 12.87 Å and is approximately the radius of the crystallite. Peaks occurring at larger distances are increasingly broadened and much less prominent. Because voids are inherent within crystallites comprising quasi amorphous systems, the amplitude of the peaks in the experimental $G(r)$ curve (figure 13) are decreased considerably and the "wash-out" region is an indication of the radius of the crystallites. There is some ambiguity as to where this "wash-out" region occurs, but it appears to be between 16 to 20 Å. As it will become evident, Ni as well as

Cu films exhibit an average crystallite radius somewhere between 16 and 20 Å, which is to a large extent (though not exclusively) a function of the catalytic sites initially deposited on the substrate prior to plating⁽¹⁵⁾. An average crystallite radius between 16 and 20 Å, indicates that the films consist of randomly oriented cubic crystallites with sides of approximately six lattice parameters in length. It is because of these inherent voids within the crystallites, that we choose to compare these experimental scattered electron intensities to theoretical ones calculated for Ni crystallites containing 343 atoms only.

Correlations between the experimental and theoretical $G(r)$ curves (figures 13 and 15 respectively) are made in order to determine the degree of strain (or lattice distortions) present in the Ni-P film obtained using metallizing bath A. The fractional error for the positions of the interatomic distances in the function $G(r)$ is estimated to be 0.05, i.e. 5%. Table 4 gives the comparison indicating a lattice distortion of $(8 \pm 5)\%$. To what extent traces of phosphorus contribute in distorting the crystallites is uncertain.

The intensity curve for the same sample heat treated for six hours at 300°C is shown in figure 16. It is seen to be slightly sharper since heat treatment promotes crystal growth. The associated reduced RDF curve is shown in figure 17 exhibiting peaks of higher amplitude, which apparently is an indication of fewer voids within the crystal lattice. Table 5 gives the comparison with the theoretical $G(r)$ indicating a lattice distortion of $(9 \pm 5)\%$.

The intensity curve for a Ni-P sample prepared using metallizing bath B, is shown in figure 18. It is expected that the scattered intensities associated with the (220) and (311) planes, will exhibit comparable amplitudes for randomly oriented Ni crystallites. The scattering associated with the (111) plane, however, should be significantly larger in amplitude relative to the scattering associated with the other planes. This can be seen by observing the theoretical intensity curve in figure 14. Figure 18 therefore suggests, that there is a preferred orientation with the (111) plane parallel to the plane of the substrate in films grown using (Nickel) metallizing bath B. Figure 19 gives the $G(r)$ curve for this sample. The first peak in this particular $G(r)$ curve should not be mistaken for the nearest neighbor distance, since this rather large oscillation is a computational artifact due to the (111) reflection being very small compared to the others when the reduced scattered intensity is computed. This is because, in the reduced scattered intensity, division by f^2 and multiplication by s magnifies peaks at larger scattering factors giving them equal weight. Table 6 gives the comparison with the theoretical $G(r)$ indicating a lattice distortion of $(5\pm 5)\%$.

Figure 12. Normalized scattered electron intensity for a Ni-P sample obtained using metallizing bath A.

Figure 13. Reduced RDF, $G(r)$ [atoms/ $\text{\AA}^3$], calculated from the intensity curve of figure 12.

Figure 14. Calculated normalized scattered electron intensity for a Ni crystallite containing 343 atoms.

Figure 15. Reduced RDF, $G(r)$ [atoms/Å³], calculated from the intensity curve of figure 14.

Table 4. Comparison of nearest and etc. neighbor distances obtained from figure 13 , with those obtained from the theoretical reduced RDF of figure 15.

Exp. [Å ± 5%]	Theor. [Å]	Exp./Theor. [± 5%]
2.59	2.49	1.04
4.77	4.36	1.09
6.02	5.40	1.11
7.16	6.54	1.09
8.40	7.68	1.09
9.34	8.92	1.05
11.00	/	/
11.73	10.79	1.09
13.80	12.87	1.07
15.25	14.32	1.06
16.50	15.05	1.10

Figure 16. Normalized scattered electron intensity for a heat treated Ni-P sample obtained using metallizing bath A.

Figure 17. Reduced RDF, $G(r)$ [atoms/Å³], calculated from the intensity curve of figure 16.

Table 5. Comparison of nearest and etc. neighbor distances obtained from figure 17, with those obtained from the theoretical reduced RDF of figure 15.

Exp. [Å ± 5%]	Theor. [Å]	Exp./Theor. [± 5%]
2.69	2.49	1.08
4.77	4.36	1.09
6.02	5.40	1.11
7.16	6.54	1.09
8.51	7.68	1.11
9.75	8.92	1.09
11.83	10.79	1.10
14.11	12.87	1.10
15.48	14.32	1.08
16.60	15.05	1.10

Figure 18. Normalized scattered electron intensity for a Ni-P sample obtained using metallizing bath B.

Figure 19. Reduced RDF, $G(r)$ [atoms/ $\text{\AA}^3$], calculated from the intensity curve of figure 18.

Table 6. Comparison of nearest and etc. neighbor distances obtained from figure 19, with those obtained from the theoretical reduced RDF of figure 15.

Exp. [Å ± 5%]	Theor. [Å]	Exp./Theor. [± 5%]
2.59	2.49	1.04
3.84	/	/
4.57	4.36	1.05
5.81	5.40	1.08
6.95	6.54	1.06
8.09	7.68	1.05
9.34	8.92	1.05
10.58	/	/
11.41	10.79	1.06
13.39	12.87	1.04
14.94	14.32	1.04
15.88	15.05	1.05

10. Cu Films

The electron scattered intensity curve for an electroless Cu sample is given in figure 20. The corresponding $G(r)$ curve is given in figure 21. This is to be compared to the theoretical scattered intensity and subsequent reduced RDF curves calculated for a Cu crystallite containing 343 atoms (figures 22 and 23 respectively).

If it is assumed that traces of phosphorus are responsible for the distortion of crystallites in Ni-P samples, then we might anticipate no distortion of crystallites in Cu samples, since there is no phosphorus present in these films. Table 7 gives the comparison with the theoretical $G(r)$ indicating a lattice distortion of $(10 \pm 5)\%$, however.

The intensity curve for an electroplated Cu sample is given in figure 24. Comparison with the theoretical intensity curve (figure 22) seems to indicate that a larger percentage of the crystallites are deposited with the (111) plane parallel to the substrate surface. This is not as pronounced, however, as with the Ni-P using metallizing bath B. The corresponding $G(r)$ curve is given in figure 25. Table 8 gives the comparison with the theoretical $G(r)$ indicating a lattice distortion of $(7 \pm 5)\%$.

Table 9 shows the nearest etc. neighbor distances in bulk Ni and Cu. It was calculated and found, that nearest etc. neighbor distances given by the theoretical $G(r)$ curves for Ni and Cu (figures 15 and 23 respectively), approach bulk values as crystalline size increases and larger scattering vectors are taken into account.

Figure 20. Normalized scattered electron intensity for electroless Cu.

Figure 21. Reduced RDF, $G(r)$ [atoms/Å³], calculated from the intensity curve of figure 20.

Figure 22. Calculated normalized scattered electron intensity for a Cu crystallite containing 343 atoms.

Figure 23. Reduced RDF, $G(r)$ [atoms/Å²], calculated from the intensity curve of figure 22.

Table 7. Comparison of nearest and etc. neighbor distances obtained from figure 21, with those obtained from the theoretical reduced RDF of figure 23.

Exp. [Å ± 5%]	Theor. [Å]	Exp./Theor. [± 5%]
2.80	2.49	1.12
4.05	/	/
4.68	4.46	1.09
6.23	5.60	1.11
7.47	6.74	1.11
8.61	7.89	1.09
10.07	9.13	1.10
11.31	/	/
12.14	11.10	1.09
13.39	/	/
14.32	13.18	1.09
15.98	14.63	1.09
17.12	15.46	1.11

Figure 24. Normalized scattered electron intensity for electroplated Cu.

Figure 25. Reduced RDF, $G(r)$ [atoms/Å²], calculated from the intensity curve of figure 24.

Table 8. Comparison of nearest and etc. neighbor distances obtained from figure 25, with those obtained from the theoretical reduced RDF of figure 23.

Exp. [Å ± 5%]	Theor. [Å]	Exp./Theor. [± 5%]
/	2.49	/
3.22	/	/
/	4.46	/
5.71	5.60	1.02
7.06	6.74	1.05
8.72	7.89	1.10
10.07	9.13	1.10
11.73	11.10	1.06
13.90	13.18	1.05
/	14.63	/
16.91	15.46	1.09

Table 9. Nearest and etc. Neighbor distances in bulk Ni and Cu.

Ni [Å]	Cu [Å]
2.49	2.56
3.52	3.61
4.32	4.43
4.98	5.11
5.57	5.72
6.10	6.26
6.59	6.76
7.05	7.23
7.47	7.67
7.88	8.08
8.26	8.48
8.63	8.85
8.98	9.22
9.65	9.90
9.97	10.22
10.27	10.54
10.57	10.84
10.86	11.14
11.14	11.43
11.42	11.71
11.69	11.99
11.95	12.26
12.21	12.52
12.46	12.78
12.70	13.03
12.95	13.28

11. Ni-Cu Film

The intensity curve for the Ni-Cu sandwich is shown in figure 26. The reduced RDF for this binary system consists of four partial functions $G_{ij}(r)$. Because the Ni-Cu sandwich is only a few hundred Angstroms thick, it can be thought of as an interface so that one may suspect epitaxial growth of Cu upon Ni. If this happens, then the partial functions $G_{ij}(r)$ will give the same interatomic distances corresponding to that of a nickel crystallite. What is found, is that only interatomic distances corresponding to that of a copper crystallite are present. This is illustrated in figure 27, which compares the Ni-Cu reduced RDF to the theoretical reduced RDF calculated for Cu crystallites containing 343 atoms. The amplitude of the peaks for the Ni-Cu reduced RDF are significantly smaller compared to that of calculated Cu, indicating the presence of voids within the crystal lattice. Table 10 shows that the interatomic distances in the Ni-Cu system correspond to that of Cu, within experimental error.

Figure 26. Normalized scattered electron intensity for Ni-Cu.

Figure 27. Ni-Cu reduced RDF compared to the theoretical reduced RDF calculated for Cu crystallites containing 343 atoms.

Table 10. Comparison of interatomic distances for the Ni-Cu system with those obtained from the theoretical reduced RDF calculated for Cu crystallites containing 343 atoms.

Ni-Cu [Å ± 5%]	Theor. Cu [Å]	Ni-Cu / Theor. Cu [± 5%]
2.49	2.49	1.00
3.63	/	/
4.57	4.46	1.02
5.81	5.60	1.04
6.85	6.74	1.02
7.89	7.89	1.00
9.13	9.13	1.00
11.00	11.10	0.99
13.18	13.18	1.00
14.73	14.63	1.01
15.56	15.46	1.01
16.71	/	/

CHAPTER IV

CONCLUSION

Both Ni and Cu films appear to have an average crystallite radius between 16 and 20 Å. Sensitizing (Sn II) and activating (Pd II) the substrates prior to plating, produces a distribution of catalytic sites where metal nucleation can take place. This similarity in average crystallite radius for Ni and Cu films, is attributed to a large extent (though not exclusively) as being a function of these catalytic sites. An average crystallite radius between 16 and 20 Å indicates that the films consist of randomly oriented cubic crystallites with sides of approximately six lattice parameters in length.

Observed interatomic distances in the Ni and Cu films signify considerable distortions when compared to theory. Introduction of traces of impurity atoms such as phosphorous in Ni and dissolved hydrogen in Cu produce distortions which propagate within the crystallites. The decrease in the amplitude of the peaks in the experimental reduced RDF compared to the theoretical reduced RDF for such systems, indicates the presence of voids within the crystallites. The reduced RDF curve for a heat treated Ni-P film whose metallizing bath is A (figure 17), exhibited peaks of higher amplitude when compared to the non-heat treated reduced RDF (figure

13). Apparently, this is an indication of fewer voids, since heat treatment promotes crystallization. The effect of voids, is again to distort the crystallites. It should be noted, that the reduced RDF curves reveal only averaged effects.

Of interest is the fact that the scattered electron intensity curve for a Ni-P film prepared using metallizing bath B (figure 18), as well as for electroplated Cu (figure 23), seems to indicate a preference for the crystallites in them to be deposited with the (111) plane parallel to the substrate surface, for reasons yet unknown.

The reduced RDF for the Ni-Cu film yields interatomic distances which closely resemble that of copper alone. This could be explained if the Cu layer was significantly thicker than the Ni, but energy-dispersive x-ray spectral analysis showed the atomic percentage of the two elements to be similar, i.e. similar thickness. In free atoms of Ni and Cu, the electronic configurations are $(3d)^8(4s)^2$ and $(3d)^{10}(4s)^1$ respectively. For the Ni-Cu sandwich, at the interface valence electrons of Cu may be allowed to make transitions to (3d) bands in neighboring Ni atoms. The proportion of electrons from Cu making transitions to (3d) bands, will be considerably larger than the proportion making transitions to (4s) bands. This is a result of the density of states (number of energy states per unit volume per unit energy range) curve for a (3d) band being considerably higher and narrower than that for the (4s) band. For Ni-Cu alloys containing about 60 atomic percent Cu, ferromagnetism is no longer present⁽²⁰⁾ which is

in support of electrons from Cu in (4s) bands filling holes in the (3d) bands of Ni. The result of such transitions in the Ni-Cu sandwich, is to alter the electron concentration per unit cell in the vicinity of the interface leading to macroscopic distortions involving the whole structure. This may be the explanation as to why the reduced RDF yields interatomic distances which closely resemble that of Cu.

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