# Superlattices and Their Applications

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Abstract

I would like to make an overview of the present status of multilayer studies. Then I will show some results of our recent studies of metallic multilayers. We have synthesized Mo/Cu multilayers by alternate deposition in an U.H.V. and analyzed resistivities by considering the scattering at the interfaces and the grain boundaries. Mo/Al were also synthesized by sputtering. The in-plane resistivities were measured and negative temperature coefficients were found for the films with the wavelength less than 60A.

KEY WORDS: (Metallic Multilayer) (Resistivity)

## 1. Introduction

Recently there has been extensive interest in the properties of Layered Ultrathin Coherent Structures (LUCS)(ref.1). Sometimes they are termed Artificial Superstructure Films (ASF)(ref.2) and sometimes they are referred to as metallic superlattices or merely multilayered films. The possibility of fine tuning of band structures and novel magnetic structures etc. by artificially layering materials seems attractive and promising. As for metals, metallic multilayers have been produced over the last ten years by sputtering and electron-beam evaporation with varying degrees of success. These structures are found to exhibit a variety of interesting physical phenomena. The current interest is in how the physical properties are effected by the novel arrangement of the atoms. At present, it is not clear which material and fabrication parameters determine the growth and the properties of a superstructure in a certain metal. Consequently, it is necessary to characterize the structures intensively and explore a wide range of parameters in assessing the relationship between the physical properties and the structures.

We have synthesized metallic multilayered films by the alternate deposition of two different kinds of metals in ultra high vacuum ($10^{-9}$Torr) and rf sputtering method. We have measured the in-plane resistivity and the temperature coefficient of resistivity (TCR) as a function of the multilayer periodicity and interpreted the obtained results in terms of the effects of the scattering at the interface between copper and molybdenum layers and the scattering at the grain boundaries within the molybdenum and copper layers. We have estimated the size of the grains within the layers by comparing the

experimental results with the calculated values by Dimmich's theory of resistivity of multilayered films.

## 2. Mo/Cu

### 2.1 Sample preparation

The Mo/Cu multilayered films were prepared by electron beam deposition technique. Two electron beam evaporators are placed in a high vacuum system. Prior to deposition, the residual gas pressure in the chamber was about $5\times10^{-10}$ Torr but increased usually to $5\times10^{-9}$ Torr during evaporation. The thickness of the films and the deposition rates of molybdenum and copper were measured with two quartz crystal thickness monitors. The mechanical shutters for the alternate deposition of molybdenum and copper atoms were driven electromagnetically by these monitors and a programmable digital comparator. The deposition rates of molybdenum and copper were about 0.3A/s and 0.5A/s, respectively.

Single crystal sapphires with the (11.0) surface and p-type (100) silicon wafers were used as substrates. The substrates were held on a molybdenum plate whose temperature was controlled using a W-W:Re thermocouple inserted in the molybdenum plate and a Ta heater in a feedback loop. The temperature of the substrate can be controlled in this fashion from room temperature to approximately 1000°C. In this report the substrate temperature was varied 40°C, 80°C and 200°C.

Prior to deposition of Mo/Cu multilayered films, molybdenum buffer layer of 445A was deposited on the substrates.

### 2.2 Structure

Using CuKα radiation, We characterized the structures of films by the standard θ-2θ x-ray diffraction. X-ray analysis shows that the multilayer periods $\Lambda_x$ obtained from the observed x-ray peak positions are close to the designed values controlled by quartz crystal thickness monitors during the growth. In figure 1, the multilayer periods $\Lambda_x$ are compared with the designed values on preparation ($\Lambda_d$). The total film thickness of the multilayered films were determined by an interferometric technique. This observed thickness were also in good agreement with the designed values.

The low angle θ-2θ diffractometer scan show typically three-to fifth orders of distinct satellite peaks which come from the introduction of long periodicity or chemical order. Figure 2(a) shows the result of the low angle scan of $[Mo(98)/Cu(98)]_{25}$ on silicon substrate and figure 2(b) is that for the sapphire (1120) substrate. These multilayered films were synthesized at 40 C. Here, we have employed the notation $[Mo(d_M)/Cu(d_C)]_n$ to represent the multilayered film. The parameters $d_M$ and $d_C$ denote , respectively, the designed thickness of individual molybdenum and copper layers in the unit of Angstrom, and the total number of deposited unit bilayers of molybdenum and copper layer is expressed by n. The designed multilayer period is simply equal to $\Lambda_d=d_M+d_C$. Comparing figure 2(a) with figure 2(b), higher order satellite peaks are observed for the sapphire substrate than the silicon wafer substrate. The same results was obtained in all the specimens whose multilayer periods are in the range between 21A and 196A. The distinct satellite peaks of higher orders indicate better regularity or coherency of the stacking of the bilayers of molybdenum and copper layers. For all the specimens molybdenum buffer layer of 445A thickness was initially deposited on the substrates prior to synthesis of Mo/Cu multilayered films.

Information about the crystallinity of the multilayered films can be obtained from the x-ray scattering at high angles. The structure of a multilayer, bcc metal/fcc metal, consists of the bcc(110) planes stacking on the fcc(111) planes with random orientation within the plane of the film. In the diffraction pattern of the Mo/Cu multilayered films some peaks appeared near the (110) reflection peak of molybdenum and the (111) reflection of copper. Figure 3 show the diffraction patterns of $[Mo(11)/Cu(10)]_{70}$ and $[Mo(98)/Cu(98)]_{25}$ samples, respectively, which were deposited at the substrate temperature of 40°C. For the films with shorter wavelength, one distinct main peak appeared near the center of the (110) reflection peak of molybdenum and the (111) reflection peak of copper. On the other hand, the spectra are composed of two main peaks for large wavelength. One appears at a little higher angle than the Mo (110) reflection and the other is at the (111) reflection peak of bulk copper metal.

In the high angle region, the satellite peaks are not so distinct as those in low angles. Several kinds of multilayered films studied to date show the similar tendency that no satellite peaks can be found at the high angles but sharp satellite peaks appear in the low angle region indicating a strong composition modulation. The present results is typical for the systems with large structural mismatch between the constituents, or in the cases where one of the constituents is amorphous or disordered.

From the full width at half maximum (FWHM) of peaks in the high angle

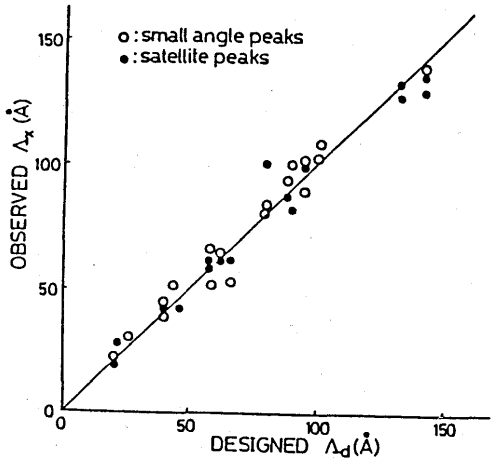
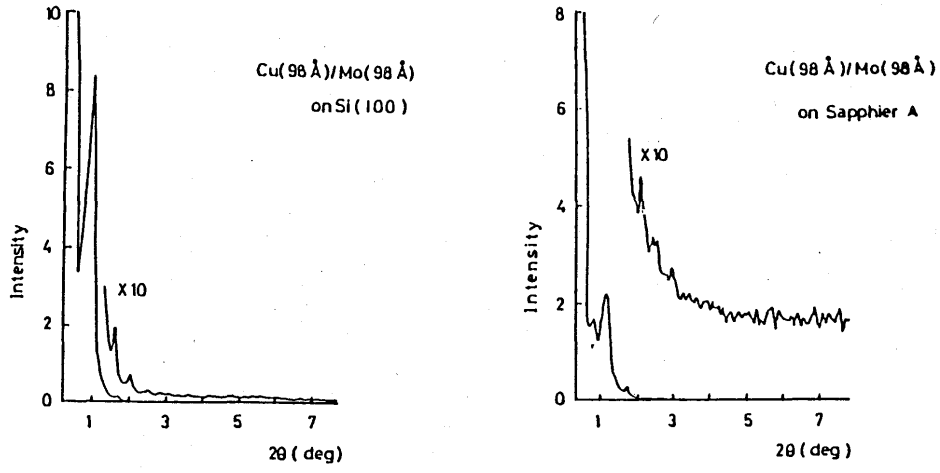



Figure 1. The relation between the multilayer period obtained from x-ray diffraction peaks $\Lambda_x$ and that designed $\Lambda_d$.




(a) (b)

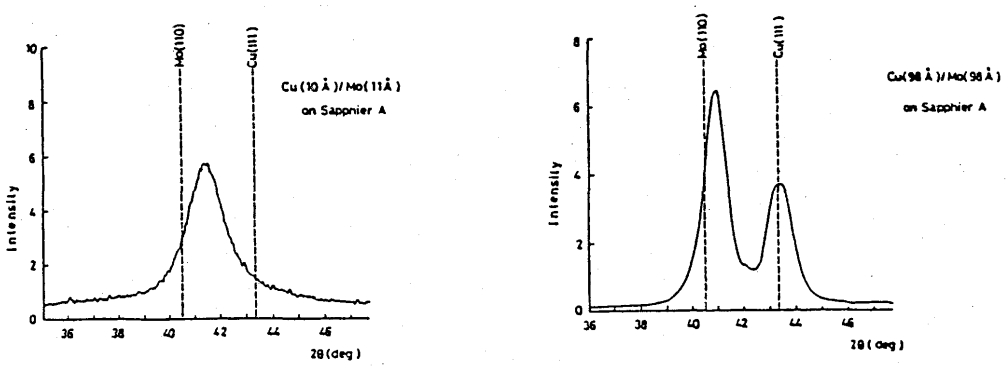
Figure 2. X-ray diffraction pattern of the low angle scan of $[Mo(98)/Cu(98)]_{25}$ on silicon substrate(a) and that for the sapphire (11.0) substrate(b).

region, one can estimate the mean grain size (coherence length) perpendicular to the layers. Figure 4 shows the mean grain size of the multilayered films deposited at 40°C, 80°C and 200°C as a function of wavelength. Comparing within the samples deposited at the same temperature, the films with longer periods have larger grain sizes. For the samples with the same multilayer period, the mean grain size was larger for the films synthesized at lower temperature.

3.3 In-plane resistivity

The temperature dependence of the in-plane electrical resistivity was measured in a liquid helium cooled cryostat operating between 3K and 280K. We measured the samples of $[Mo(11)/Cu(10)]_{70}$, $[Mo(20)/Cu(20)]_{52}$, $[Mo(29)/Cu(29)]_{42}$, $[Mo(49)/Cu(46)]_{31}$ and $[Mo(98)/Cu(98)]_{25}$ deposited on 5mmx10mm (100) silicon wafers at the substrate temperature of 40°C. Figure 5 shows the dependence of the in-plane resistivity on the inverse multilayer period at 280K and 4.2K, in which points represent the measured values. The in-plane resistivity increased with inverse multilayer period, but not monotonic. We have analyzed the electric resistivity of the Mo/Cu multilayered films by Dimmich's theory(ref.3).

According to Dimmich's theory, it is assumed that both metals have isotropic and the Fermi energies of two metals are sufficiently close to neglect the contact potential difference arising at the interfaces. Two main




(a) (b)

Figure 3. X-ray diffraction pattern obtained from $[Mo(11)/Cu(10)]_{70}$ (a) and $[Mo(98)/Cu(98)]_{25}$ samples in the vicinity of Bragg diffraction from Mo(110) and Cu(111) planes.

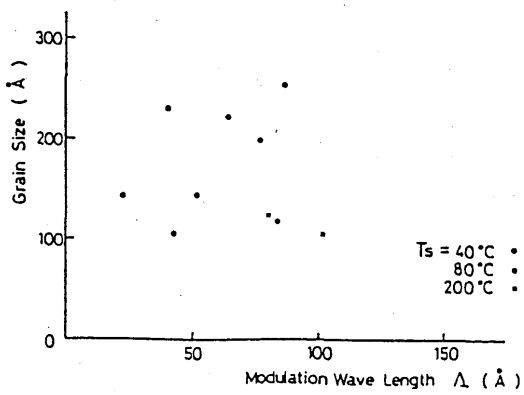



Figure 4. The multilayer period dependence of the mean grain size of the multilayered films deposited at 40°C, 80°C and 200°C.

mechanisms of the scattering of conduction electrons were took into account. One is the scattering at the interfaces which can be described by introducing the transmission parameter P. P is the probability of the coherent passage of an electron across an interface. The other mechanism is the scattering at the grain boundaries within each layer. Mayadas and Shatzkes represented the grain boundaries as parallel, partially reflecting planes, perpendicular both to the electrical field and to the plane of the layers. they are randomly placed with average distances b. The grain -boundary-limited relaxation time $\tau^*$ was expressed in the form

$$1/\tau^* = 1/\tau \times (1 + k_F/|k_{Fx}|) \quad (1)$$

where

$$\alpha = \lambda/b \times R/(1-R) \quad (2)$$

and $\tau$ is the bulk relaxation time in each layer, R is the reflection coefficient for electron striking a grain boundary in the metal, $k_F$ is the magnitude of the Fermi wavevector and $k_{Fx}$ is the x component of the wave vector where the x direction is parallel to the filed, respectively. Here, the grain boundary scattering is included in the relaxation times in each layers.

The bulk relaxation times in the molybdenum and copper layers were computed by the free electron model. For convenience of the calculations, the transmission parameter P was assumed to be the same values in the case of crossing an interface of electron from a molybdenum layer to a copper layer and in the opposite case. It was also assumed that the thickness, masses of conduction electrons, the reflection coefficient at grain boundary R and average distance of grain boundaries are the same for the layers of molybdenum and copper metals.

In figure 5, the solid line (a) and (b) represent the computed values of the resistivities. The obtained values could be fitted by these two lines well with the observed values, when we chosen the scattering parameters of P=0 and R=0.3 in both lines. In the calculation of solid line (a) the average grain size b parallel to the layers was proportional to multilayer period, b=0.3x$\Lambda$. In the line (b) the grain size b is constant at 20A, b=20A.

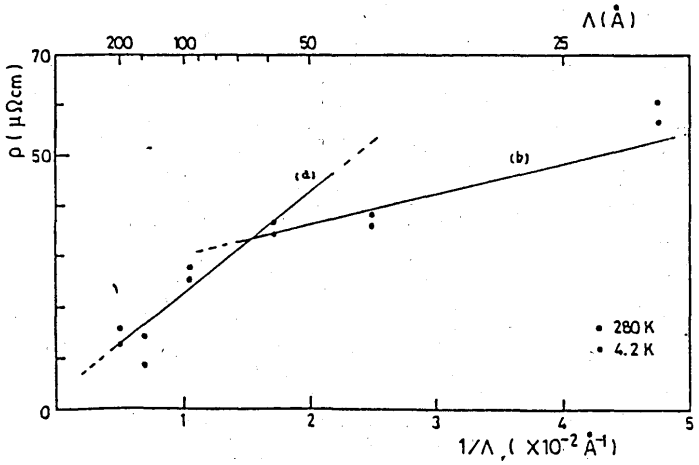



Figure 5. The in-plane resistivity of Mo/cu films. Points: measured values. Solid curves: calculated fit, using Dimmich's theory. (a):P=0,R=0.3,b=0.3x$\Lambda$ . (b):P=0,R=0.3,b=20A.

Taking no account of the scattering at the grain boundaries, the calculated values were rather lower than the observed values. So we should take into account the boundary scattering. If the grain size was assumed to be constant, the gradient of the calculated line of resistivities vs inverse multilayer period could be fitted in the short multilayer-period region. But in the long period region the gradient were too small for the whole range of the scattering parameters. We need two calculated lines to fit the observed values in all the multilayer-period region. In the long period region the average grain size parallel to the layers was proportional to the multilayer period. when the multilayer period was shorter than 60A, the grain size became 20A and kept it constant. In all region the transmission parameter at the interfaces was zero,P=0. This means that any conduction electron do not pass coherently through the interfaces. It is consistent with the result of the structural studies that some kinds of disordered or amorphous-like layers exist at the interfaces between molybdenum and copper layers.

## 3. Mo/Al

### 3.1 Sample preparation

Mo/Al multilayers were prepared by alternating sputtering deposition of Mo and Al. The two particle fluxes are shielded from each other so that no overlap of the fluxes occurs. Substrates were fixed on a rotating turntable so as to pass over the two fluxes in turn. The substrates used in this study were Si(110), Si(111), and Corning 7059 glasses.

A series of experiments were performed by systematic varying the sputtering rate, pressure, and substrate temperature to obtain a high degree of texture and possibly epitaxy. The degrees of texture were almost the same for all substrates. The initial pressure of vacuum chamber was $2\times10^{-6}$ Torr. The sputtering argon gas pressure was between 5 mTorr and 20 mTorr and the deposition rate was between 70 and 170 A/min. After determining the conditions for the highest degree of texture, samples with equal and unequal layer thicknesses, fixing the ratios of the individual layer thicknesses of Mo and Al layers at 1:1, 1:3, and 3:1, were fabricated. The modulation wavelength ( $\Lambda$ ) was controlled by varying the rotation speed of the turntable from sample to sample.

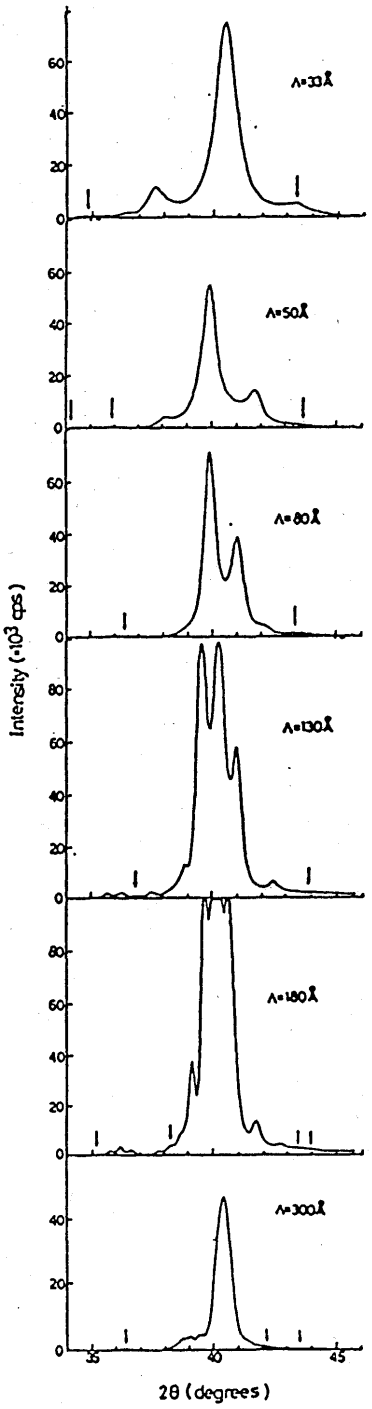



Figure 6. X-ray diffraction intensity spectra for a series of Mo/Al multilayers.

For samples with large wavelengths the argon gas pressure was 5 mTorr and for small values 10 mTorr. In the case of higher argon gas pressure, the kinetic energies of injecting atoms are lower due to collisions and thermalization with sputtering gas and the deposition rates are also smaller, which is a more suitable condition for fabricating samples with small wavelengths.

The wavelengths were determined by x-ray diffraction methods. The resulting wavelengths are in satisfactory agreement with the ones estimated from the deposition rates in the same condition.

3.2 Structure and in-plane resistivities

Standard x-ray diffraction using Cu-Kα radiation was used to determine the structures and the wavelengths of the films. Figure 6 shows the x-ray intensities obtained for equal layer thickness samples, examined in the θ-2θ geometry. For large Λ two broad lines appear, corresponding to the (110) crystal planes of Mo and the (111) planes of Al. For lower values of Λ the spectrum is composed of a central line which corresponds to the average interatomic spacing, surrounded by several modulation satellites. When Λ is less than 200A, the x-ray peaks are reasonably sharp, indicating good crystallization perpendicular to the films. However when Λ is less than 20A, no satellites can be observed and only small central peaks appear, but they are still reasonably sharp and moreover the superlattice reflections are clear.

For Λ>40A the satellites on the plus side are larger than those on the minus side. This is in good agreement with the theory of x-ray diffraction of compositionally modulated structures. The results shown that when the heavier atom (Mo) has smaller interatomic spacing than lighter atom (Al), the satellites on the plus side are always much more intensive than those on the minus side. However, for Λ <40A, the satellites on the minus side are more intensive than those on the plus side.

For all wavelengths the width of the rocking curve was nearly constant (about 4deg), which means that films are polycrystalline with the grains highly oriented in the growth direction. Below 20A no peaks can be observed, which indicates the disappearance of a textured structure.

Figure 7 shows the change of the position of the central peak which

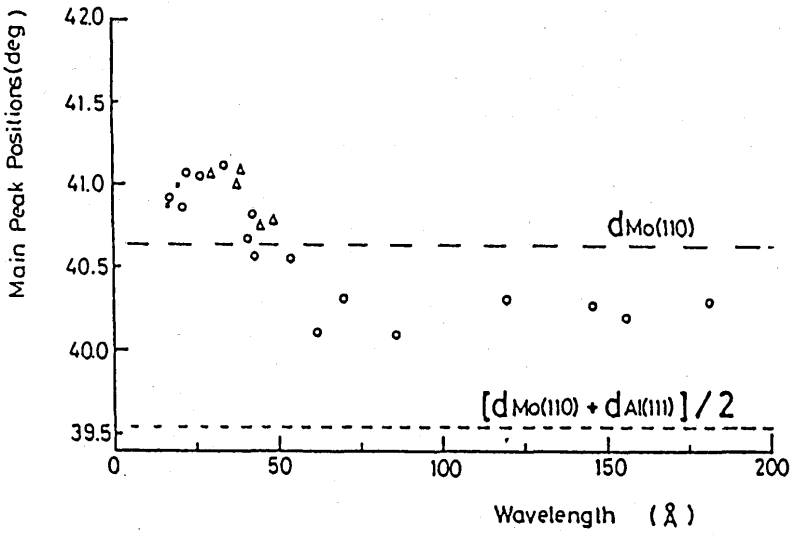



Figure 7. The position of the central peak vs the modulation wavelength.

corresponds to the average spacing (d) perpendicular to the film. For large $\Lambda$, d is a constant and it begins to decrease at about 60A. At about 40A the decrease in d stops and when is less than 40A, d becomes another constant again. Below 25A, d increases slightly, which may be due to the loss of the integrity of texture, namely disorder within grains which appears as a broadening of the width of the x-ray rocking curve. Experimentally determined d's are smaller than the average spacing of bulk Mo(110) and Al(111), indicating that the films are compressed normal to film surface.

The Full Width at Half Maximum (FWHM) of the central peak increases drastically for $35A < \Lambda < 60A$. For $\Lambda < 60A$ the FWHM's were 0.32deg, which corresponds to the instrumental resolution of the x-ray equipment, and for $\Lambda < 35A$ they were 0.38deg. As the grain size decreases monotonically with decreasing layers thickness, we can conclude that the increase of FWHM is not due to the decreasing in grain size. The reason for this maximum is supposed to be misfit-dislocations at interfaces or formations of intermetallic compounds. The latter is less probable because in the x-ray diffraction simulation(ref.4) no inversion of the intensities of x-ray satellites occurs by formations of some simple intermetallic compounds.

The in-plane resistivities were measured and negative temperature coefficients of resistivity (TCR) were found(ref.5,6) for the films with $\Lambda < 60A$. The gradual change of the resistivity with the modulation wavelength must be imposed by the structural change of the multilayered film.

This work was performed in collaboration with Dr. T. Izumiya, Mr. T. Kaneko, Mr. T. Sasaki, Mr. A. Yamaguchi, Miss M. Sakuda and Prof. M. Doyama.

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