JOURNAL OF MATERIALS SCIENCE 32 (1997) 2605–2609

X-ray characterization of annealed Cu/Ni multilayers

S. JAYAKODY, J. CHAUDHURI
Department of Mechanical Engineering, Wichita State University, Wichita, KS 67208, USA
A. F. JANKOWSKI
Lawrence Livermore National Laboratory, Livermore, CA 94550, USA

A detailed study has been made of the X-ray characterization of Cu/Ni multilayers. Different mathematical models have been used to calculate the X-ray diffraction intensity and theoretical and experimental profiles were compared. An extended step model, which incorporates repeat-period fluctuations, and a model for interdiffusion were used. By varying the repeat-period fluctuation, the theoretical X-ray profile obtained from the extended step model was compared with the experimental curve. A best fit was obtained for a 1.6% fluctuation in the repeat period. For the second model, Cu/Ni samples annealed for different times (i.e. 2, 6, 14 and 20 h) were considered. The experimental values of the amplitudes of the first and second harmonics of the interplanar spacing were compared with the theoretical values. A coherent interface is predicted for the un-annealed sample. It is observed that the longer the annealing time, the higher is the interdiffusion. The interplanar spacing of the multilayers approaches the average interplanar spacing of the homogeneous Cu/Ni mixture with the longer annealing time (i.e. 20 h).

1. Introduction

The last two decades have seen rapid developments of thin film technology. The engineering of materials with novel physical properties by artificially layering metals and semiconductors has been extensively studied. A large amount of work has been published concerning the structure and properties of metallic multilayers. They are fabricated by alternately depositing layers whereby a one-dimensional composition modulation is produced.

The structural refinement of the multilayers is very important. The presence of the additional periodicity of the layered material often contributes to an increase in elastic moduli [1, 2], as well as valuable magnetic [3], transport and superconducting properties. By changing the material at each layer and the layer thicknesses, it is possible to optimize desired properties of the system. Many applications for multilayers are being pursued, including mirrors for X-rays and neutrons, high-critical-current superconductors, magneto-resistive heads, and magneto-optical recording materials. Multilayers are useful systems for studying thin films, interfaces, and inter-layer coupling effects, because samples of large volume can be prepared and surface contamination can thus be avoided. Many physical properties depend sensitively on structural properties such as interdiffusion, crystallinity, strain and roughness, making structural characterization a precondition to understanding the physical properties. Multilayers are usually fabricated by deposition techniques such as sputtering or evaporation, and are not in thermodynamic equilibrium. Therefore, the structure is strongly dependent on growth conditions.

The foundation of any understanding of multilayer properties must be in the structure and characteristics at the interface. The X-ray diffraction technique can be used to investigate the structure and interfacial characteristics of the multilayers. It is non-destructive and provides structural information on the atomic scale. The evolution of one-dimensional order along the growth direction can be studied on a standard diffractometer. The positions and line shapes of the Bragg reflections of the average lattice and of the surrounding satellite reflections can be used to calculate the average lattice constants and the average modulation wavelength or repeat-period, and to obtain a measure of fluctuations in both quantities that may be caused by composition gradients and loss of coherence.

In this study, Cu/Ni multilayers are analysed using X-ray diffraction theories. Consideration of imperfections during fabrication, and interdiffusion can be achieved by appropriate mathematical models. The first model (an extended step model) [4] incorporates an interfacial fluctuation. The second model [5] facilitates the investigation of the interdiffusion characteristics of Cu/Ni multilayers. A simplified expression for the amplitude of the scattering is formed and introduced in this paper. The intensities of the satellite peaks are proportional to the Fourier components of the direct space composition modulation. Therefore, the interdiffusion of Cu and Ni can be studied by measuring the satellite intensities as a function of annealing time at a constant temperature.

2. Experimental procedure

The Cu/Ni multilayers are prepared by planar magnetron sputter deposition [2]. The deposition chamber is cryogenically pumped to a base pressure of 6.5×10^{-6} Pa. Two magnetron sources are horizontally placed 9 cm away from the facing circumference of a stainless steel substrate table. An argon gas pressure is used to sputter the target materials with purity greater than 99.9994%. The mass flow rate of the argon is 20.4 $cm^3\ min^{-1}$. The Cu and Ni magnetron sources are operated in the d.c. mode at 190–210 and 250–400 V discharges, respectively. Using 6 MHz quartz crystal microbalances, the instantaneous deposition rates are calibrated to the applied target power. The deposition rates for Cu and Ni are 1.0 and 1.6 nm s^{-1}, respectively. Each layer pair is fabricated to have an equal number of Cu and Ni atomic planes. The experimental X-ray diffraction curves are obtained using a Philips diffractometer with a graphite monochromator placed before the detector and tuned for the CuK_α radiation. The [1 1 1] reflection was used.

3. Analysis

3.1. An extended step model

Preliminarily a step model [5, 6] was used to obtain theoretical X-ray diffraction profiles. Considering the comparison of theoretical and experimental X-ray profiles in Fig. 1, it is possible to conclude that they are very close to each other. The angular position and the height of the experimental 0th order peak as well as satellite peaks are as predicted by the theory. However, the experimental peaks are broader than the theoretical one which could be due to the fluctuation of the repeat-period. The X-ray line broadening due to repeat-period fluctuation is considered in the extended step model. The step model is formed under the assumption that there is a complete alternation of chemical composition at the Cu/Ni interface and no fluctuation of the multilayer modulation is present. Pragmatically, it is very hard to follow these assumptions. Therefore, some deviations from an idealized model can be expected.

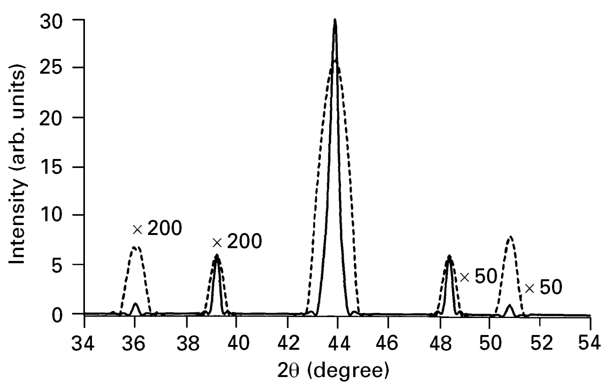

Figure 1 Experimental (- - -) and theoretical (———) X-ray diffraction profile comparison using the step model; [1 1 1] reflection.

The extended step model [4] incorporates the variation of the superlattice period and assumes that the superlattice is nearly ideal. There have been several models proposed [7–12] to explain the variation quantitatively. This assumes a Gaussian distribution of the fluctuation in its superlattice period and a complete alternation of chemical composition at the interface. The diffracted intensity $I(K)$ is given by,

$$I(K) = (P)L(K)|F(K)|^2 \tag{1}$$

where P is the Lorentz-polarization factor, $L(K)$ and $F(K)$ are the modified Laue function and the structure factor, respectively, and are expressed as

$$L(K) = \frac{1 + \exp(-N\rho^2K^2/2) - 2\exp(-N\rho^2K^2/4)\cos(N\Delta_0 K)}{1 + \exp(-\rho^2K^2/2) - 2\exp(-\rho^2K^2/4)\cos(\Delta_0 K)} \tag{2}$$

$$F(K) = \sum_{j=1}^{n} f_j(K)\exp(iKZ_j)\exp(-d_j^2\rho_j^2K^2/16) \tag{3}$$

The Lorentz-polarization factor is

$$P = \frac{1 + \cos^2\theta}{\sin^2\theta\cos\theta} \tag{4}$$

where N is the number of bilayers, $f_j(K)$ is the atomic scattering factor times the atomic density in the nth plane, Z_j is the distance from the 0th layer to the nth layer, K is expressed as $K = 4\pi\sin\theta/\lambda$, λ is the X-ray wavelength and θ is the angle of incidence.

The superlattice repeat-period Δ is expressed as

$$\Delta = (n)d_{Cu} + (m)d_{Ni} + d_I \tag{5}$$

where d_{Cu}, d_{Ni} are interplanar spacings of Cu(1 1 1) and Ni(1 1 1) planes, d_I is the interfacial spacing and n and m are the number of Cu and Ni planes within one repeat-period. The fluctuation of Δ is considered to originate from the distribution of m and n. A Gaussian distribution, given by $\exp[-(\Delta-\Delta_0)^2/\rho^2]$, is assumed to represent the fluctuation of Δ, where Δ_0 is the average of the superlattice repeat-period. The degree of fluctuation is represented as a full width at half maximum of the Gaussian distribution and expressed as

$$\frac{\Delta - \Delta_0}{\Delta_0} = \frac{2(ln2)^{1/2}\rho}{\Delta_0} \tag{6}$$

The following data have been used for the analysis: interplanar spacing modulation of Cu(1 1 1) and Ni(1 1 1), $d_{Cu} = 0.2087$ nm and $d_{Ni} = 0.2034$ nm; interfacial spacing, $d_I = 0$ nm; number of Cu and Ni layers within each bilayer, $n_{Cu} = n_{Ni} = 5$; total number of

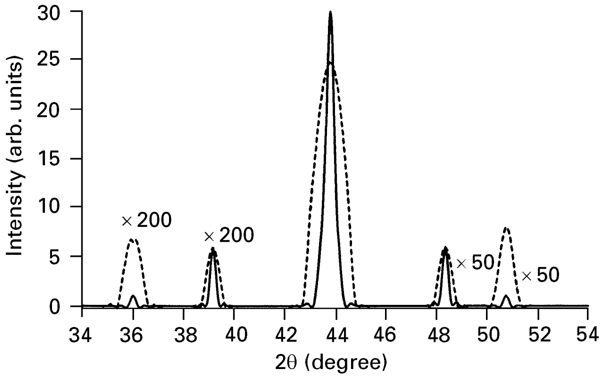

Figure 2 Experimental (- - -) and theoretical (———) X-ray diffraction profile comparison using the extended step model with $\rho = 0.1$; [1 1 1] reflection.

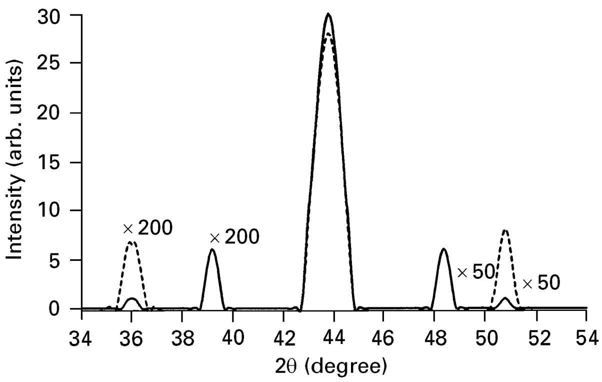

Figure 3 Experimental (- - -) and theoretical (———) X-ray diffraction profile comparison using the extended step model with $\rho = 0.2$; [1 1 1] reflection.

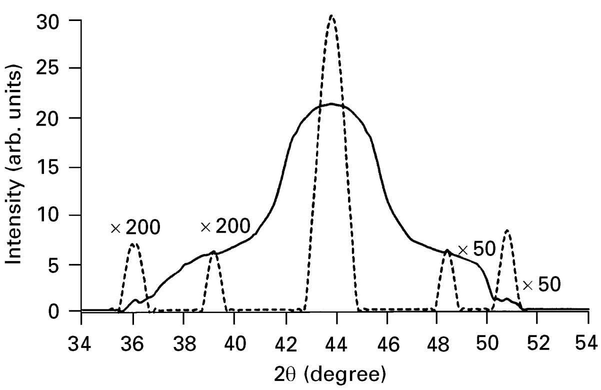

Figure 4 Experimental (- - -) and theoretical (———) X-ray diffraction profile comparison using the extended step model with $\rho = 0.3$; [1 1 1] reflection.

bilayers, $N = n_{Cu} + n_{Ni} = 10$; and average multilayer modulation spacing or repeat-period $= \Delta_0 = 2.06$ nm.

Figs 2 through 4 show a comparison of theoretical curves with the experimental ones for $\rho = 0.1$, 0.2 and 0.3 for the multilayer samples we are studying. According to the results the theoretical curve is very close to the experimental one when $\rho = 0.2$. The corresponding fluctuation of repeat-period is only 0.0334 nm or 1.6%. The fabrication of samples with a fixed multilayer modulation is very unrealistic. Therefore, some fluctuations of the multilayer modulation can be expected. An X-ray line broadening can occur with an increase of modulation fluctuation. The 1.6% fluctuation of the multilayer modulation indicates that the samples we used are of very good quality. In addition, the interfacial spacing, d_I, was considered to be zero in the analysis which shows that the interfacial fluctuation is very small in these samples.

3.2. The model which incorporates interdiffusion

The annealed Cu/Ni samples facilitate the investigation of the characteristics of the multilayers when interdiffusion is incorporated. The interdiffusion of Cu/Ni multilayers increases with the annealing time. Fig. 5 shows a comparison of the experimental X-ray profiles of the samples annealed at 0, 2, 6, 14 and 20 h, respectively. It can be seen that the intensity of the satellite peaks decreases with the annealing time.

The preceding idealized models with a square wave modulation are only achieved in systems in which the two components are immiscible under the conditions of growth. More generally there is interdiffusion, and the resulting composition and displacement waves are intermediate between a square wave and a sine wave. In the general case, the scattering amplitudes are approximated by Fourier series expansions with Bessel functions, but the expressions become sufficiently complex [5]. Thus the scattering amplitudes have been limited to truncating the Bessel function expansions to terms up to second order.

An extensive expression for the scattering amplitude of the mth order satellite peak is given by [13],

$$A_m = f_0 \sum_{j=1}^{N} \sum_{p,s=-\infty}^{\infty} J_p(\Delta_1 N) J_s(\Delta_2 \frac{N}{2}) \sum_n \phi_n \exp(2\pi ij(l + m/N + n/N + p/N + 2s/N)) \quad (7)$$

The spacing between (n-1)th and nth lattice plane is given by

$$d_n = d_0(1 + \Delta_1 \cos 2\pi n/N + \Delta_2 \cos 4\pi n/N) \quad (8)$$

The variation of the composition also causes a variation of structure factor whose value for the nth plane is given by

$$F_n = F_0(1 + \phi_1 \cos 2\pi n/N + \phi_2 \cos 4\pi n/N) \quad (9)$$

where $\phi_n =$ amplitude of the nth harmonic of the composition modulation; Δ_1, Δ_2 = amplitude of the first and second harmonics of the interplanar spacing; N = total number of layers in one bilayer or repeat-period; $|p|$, $|s| \leq 3$ is needed, if third order satellites need to be considered; $J_p = p$th integer order Bessel function; f_0 = average layer form factor; and F_0 = average layer structure factor.

The amplitude of the zero order superlattice and first, second and third order satellites are expressed in a simplified form for the first time in this paper as

$$A_0 = f_0 \sum_{j=1}^{N} \sum_{p,s=-4}^{4} J_p(\Delta_1 N) J_s(\Delta_2 N/2) (\{\exp[2\pi ij(1 + p/N + 2s/N)]\} + \phi_1\{\exp[2\pi ij(1 + p/N + 2s/N)]$$

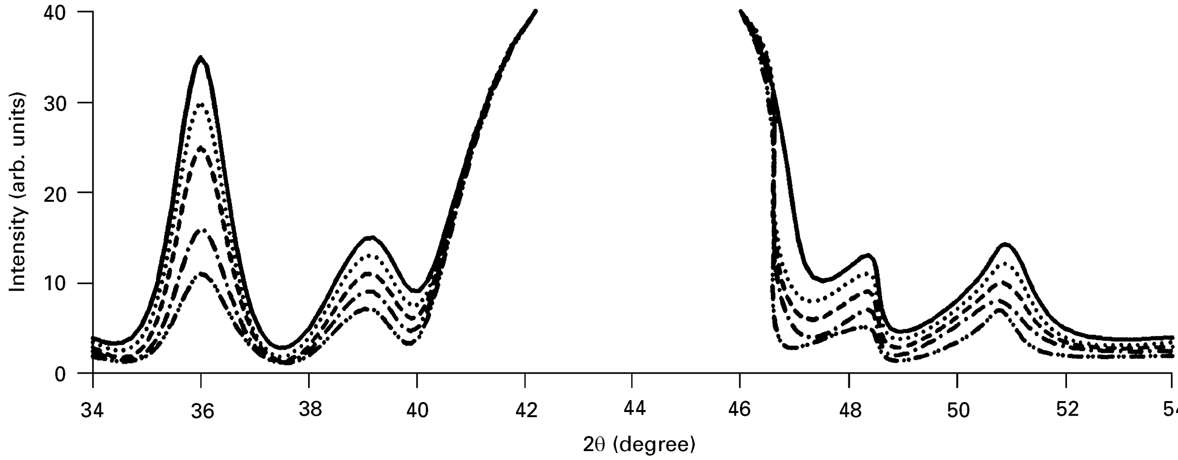

Figure 5 X-ray diffraction curves for multilayers annealed at different annealing times; [1 1 1] reflection and only first order satellites are shown. Key: ———0 h; - - - 2 h; - - - 6 h; —·—·—14 h; —··—··—20 h.

$$+ \exp[2\pi ij(1 + p/N + 2s/N)]\}$$
$$+ \phi_2\{\exp[2\pi ij(1 + p/N + 2s/N)]$$
$$+ \exp[2\pi ij(1 + p/N + 2s/N)]\}) \tag{10}$$

$$A_{\pm 1} = f_0 \sum_{j=1}^{N} \sum_{p,s=-4}^{4} J_p(\Delta_1 N) J_s(\Delta_2 N/2)$$
$$(\{\exp[2\pi ij(1 \pm 1/N + p/N + 2s/N)]\}$$
$$+ \phi_1\{\exp[2\pi ij(1 \pm 1/N + 1/N + p/N + 2s/N)]$$
$$+ \exp[2\pi ij(1 \pm 1/N - 1/N + p/N + 2s/N)]\}$$
$$+ \phi_2\{\exp[2\pi ij(1 \pm 1/N + 2/N + p/N + 2s/N)]$$
$$+ \exp[2\pi ij(1 \pm 1/N - 2/N + p/N + 2s/N)]\}) \tag{11}$$

$$A_{\pm 2} = f_0 \sum_{j=1}^{N} \sum_{p,s=-4}^{4} J_p(\Delta_1 N) J_s(\Delta_2 N/2)$$
$$(\{\exp[2\pi ij(1 \pm 2/N + p/N + 2s/N)]\}$$
$$+ \phi_1\{\exp[2\pi ij(1 \pm 2/N + 1/N + p/N + 2s/N)]$$
$$+ \exp[2\pi ij(1 \pm 2/N - 1/N + p/N + 2s/N)]\}$$
$$+ \phi_2\{\exp[2\pi ij(1 \pm 2/N + 2/N + p/N + 2s/N)]$$
$$+ \exp[2\pi ij(1 \pm 2/N - 2/N + p/N + 2s/N)]\}) \tag{12}$$

$$A_{\pm 3} = f_0 \sum_{j=1}^{N} \sum_{p,s=-4}^{4} J_p(\Delta_1 N) J_s(\Delta_2 N/2)$$
$$(\{\exp[2\pi ij(1 \pm 3/N + p/N + 2s/N)]\}$$
$$+ \phi_1\{\exp[2\pi ij(1 \pm 3/N + 1/N + p/N + 2s/N)]$$
$$+ \exp[2\pi ij(1 \pm 3/N - 1/N + p/N + 2s/N)]\}$$
$$+ \phi_2\{\exp[2\pi ij(1 \pm 3/N + 2/N + p/N + 2s/N)]$$
$$+ \exp[2\pi ij(1 \pm 3/N - 2/N + p/N + 2s/N)]\}) \tag{13}$$

Using another model [14, 15] the composition modulation can be expressed by a Fourier sum of the direct space

$$C(z) = C_{Cu}[1 + \sum_m \phi_m \cos(mkz)] \tag{14}$$

where $C(z)$ is the variation of Cu concentration with depth z and C_{Cu} is the average Cu concentration. Similarly, the modulation of interplanar spacing may be given by,

$$d_n = d[1 + \sum_m \varepsilon_m \phi_m \sin(mknd)] \tag{15}$$

where d is the average interplanar spacing and $k = 2\pi/\lambda_{\mathrm{mod}}.\lambda_{\mathrm{mod}}$ is the thickness of bilayer or the multilayer repeat-period.

Δ_m is calculated from F_{m^+} and F_{m^-} (the normalized amplitude of the $\pm m$th order satellites) values obtained experimentally.

$$\phi_m = 2\frac{(F_{m-}q_{m^+} - F_{m^+}q_{m-})}{(q_{m^+}\eta_- + q_{m^-}\eta_+)} \tag{16}$$

$$\varepsilon_m = \frac{mk\ (F_{m-}\eta_+ + F_{m^+}\eta_-)}{2\pi(F_{m-}q_{m^+} - F_{m^+}q_{m-})} \tag{17}$$

$$\Delta_m = \phi_m \varepsilon_m \tag{18}$$

where ε_m = amplitude of the interplanar spacing modulation, $q_{m\pm} = 1/d \pm mk$, $\eta_\pm = \Delta F_{m\pm}/F(h\,k\,l)$ and $F^2_{m\pm} = I_{m\pm}/I_0$, where $I_{m\pm}$ are the intensities of the mth order satellite peak, I_0 is the intensity of the zero order peak and $F(h\,k\,l)$ is the structure factor of the 0th order peak.

The Δ_1 and Δ_2 values were calculated from the experimental values of $I_{m\pm}$ (intensity of $\pm m$th order satellite peaks) and I_0 (intensity of the 0th order superlattice peak) to obtain F_{m^+} and F_{m-} and then by using Equations 16, 17 and 18. The Δ_1 and Δ_2 values thus obtained (i.e. experimental) can be compared with the values calculated using Equations 10 through 12 (i.e. theoretical). The following data have been used for the analysis.

The Bragg angle for the zero order multilayer peak $= 43.95°$.
Multilayer modulation spacing or repeat-period $= 2.06$ nm.

TABLE I Δ_m, ϕ_m and ε_m values of Cu/Ni samples for different annealing times

	Annealing time (h)				
	0	2	6	14	20
ε_1	0.040	0.033	0.020	0.010	0.005
ε_2	0.082	0.070	0.055	0.041	0.029
ϕ_1	1.051	0.831	0.551	0.221	0.121
ϕ_2	0.231	0.171	0.091	0.023	0.010
Experimental					
Δ_1	0.0420	0.0271	0.0110	0.0021	0.0006
Δ_2	0.0201	0.0120	0.0050	0.0009	0.0003
Theoretical					
Δ_1	0.0410	0.0200	0.0150	0.0070	0.0050
Δ_2	0.0310	0.0160	0.0100	0.0010	0.0009

Interplanar spacings of Cu and Ni: $d_{Cu} = 0.2087$ nm, $d_{Ni} = 0.2037$ nm.
Number of Cu and Ni layers within a bilayer: $n_{Cu} = n_{Ni} = 5$.
Total number of bilayers $= 10$.

The results are shown in Table I. It can be seen that the Δ_1 and Δ_2 values predicted by the theory are very close to the experimental values. ε_1 (the amplitude of the first harmonic of the interplanar spacing modulation) value for the 0 h annealing (no annealing) is 0.042 indicating a coherent Cu/Ni interface [16]. It can be inferred from the results that the amplitude of the first and second harmonics of the interplanar spacing decreases with the annealing time (Table I). The Cu and Ni atoms get mixed with each other due to diffusion and Cu/Ni multilayer system becomes a homogeneous composition of Cu and Ni at the longest annealing time (20 h). The interplanar spacing tends to become a constant with a longer period of annealing time since ε_1 and ε_2 are very close to zero. This constant is the average interplanar spacing of Cu and Ni (i.e. 0.2067 nm).

4. Conclusions

This paper is primarily concerned with the X-ray characterization of Cu/Ni multilayers. The X-ray diffraction profiles were obtained experimentally and compared with the theoretical values. An extended step model for fluctuations of multilayer modulation, and a model for interdiffusion are used. The X-ray diffraction profile from the sample without annealing was used to compare with the extended step model. It is possible to come to a conclusion that the samples are properly fabricated and the fluctuation of modulation or repeat-period is very small (i. e. 0.0334 nm or 1.6% of the repeat-period). By using the extended step model, the intensity line broadening is observed with increasing fluctuation which is unexplainable by the ordinary step model.

The interdiffusion has been totally ignored in the step model and extended step model, but is taken into account in the second model. A formula for the computation of the zero order and satellite peaks is mentioned in a very convenient form for the first time. Five Cu/Ni samples (annealed at 0, 2, 6, 14 and 20 h) are considered to investigate interdiffusion and the first and second harmonics of the interplanar spacing modulation are calculated. The experimental values of the first and the second harmonics of the interplanar spacing modulation were compared with the theoretical ones and close agreement was found. The first harmonic of the interplanar spacing modulation for the un-annealed sample indicates a coherent interface. The values of the first and second harmonics of the interplanar spacing modulation decreases with annealing time due to diffusion of Cu and Ni into each other.

References

1. W. A. C. YANG, T. TSAKALAKOS and J. E. HILLIARD, *J. Appl. Phys.* **48** (1977) 876.
2. A. F. JANKOWSKI, E. M. SEDILLO and J. P. HAYES, *Jpn. J. Appl. Phys.* **33** (1994) 5019.
3. B. THALLER, J.B. KETTERSON and J. E. HILLIARD, *Phys. Rev. Lett.* **31** (1978) 336.
4. M. SOHMA, K. KAWAGUCHI and Y. FUJI, *J. Appl. Phys.* **75** (1994) 1952.
5. A. SEGMUELLER and A.E. BLAKESLEE, *J. Appl. Crystallogr.* **6** (1973) 19.
6. D. B. McWHAN, in "Synthetic Modulated Structures", edited by L. L. Chang and B. C. Giesen (Academic Press, Inc., New York, 1985) p. 43.
7. E. FULLERTON, I. SCHULLER, H. VANDERSTRAETEN and Y. BRUYNSERAEDE, *Phys. Rev. B* **45** (1992) 9292.
8. D.B. McWHAN, M. GURVITCH, J. M. ROWELL and L. R. WALKER, *J. Appl. Phys.* **54** (1993) 3886.
9. N. NAKAYAMA, K. TAKAHASHI, T. SHINJO, T. TAKADA and H. ICHINOSE, *Jpn. J. Appl. Phys.* **25** (1986) 552.
10. W. SEVENHANS, M GIES, Y. BRUYNSERAEDA, H. HOMMA and I. K. SCHULLER, *Phys. Rev. B* **34** (1986) 5955.
11. B. RODMAQ, *J. Appl. Phys.* **70** (1991) 4194.
12. Y. FUJI, T. OHNISH, T. ISHIHARA, Y. YAMADA, K. KAWAGUCHI, N. YAKAYAMA and T. SHINJO, *J. Phys. Soc. Jpn.* **55** (1986) 251.
13. P. C. CHOW, A. VIGILANTE, S. C MOSS, J. T. ZBOROSKI, T. D. GOLDING and H. D. SHIH, *Mater. Res. Symp. Proc.* **208** (1991) 219.
14. R. M. FLEMMING, D.B. McWHAN, A. C. GOSSARD, N. WIEGEMANN and R. A. LOGAN, *J. Appl. Phys.* **51** (1980) 357.
15. J. CHAUDHURI, S. M. ALYAN and A. F. JANKOWSKI, *Thin Solid Films* **219** (1992) 63.
16. E. M. GYORGY, D. B. McWHAN, J. F. DILLON, JR, L. R. WALKER and J. V. WASZCZAK, *Phys. Rev. B* **25** (1982) 6739.

Received 4 June and accepted 23 October 1996