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An x-ray diffraction study on Cu–Ti metallic multilayers

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Abstract. An x-ray diffraction and computer-simulation study of Cu–Ti metallic multilayers is presented. The results show Cu–Ti artificial metallic multilayers made by magnetron sputtering technique are metallic superlattices with high structure order. An obvious even extinction phenomenon in the x-ray patterns was found and used in the analyses. Taking into account the structural coherence length perpendicular to the layers and the layer-thickness fluctuation in every period, the calculated x-ray diffraction curves are in good agreement with those measured.

1. Introduction

In recent years there has been renewed interest in artificial metallic multilayers, because some unique features have been discovered (including superconductivity, magnetism and elastic behaviour). In order to understand these properties, many structural studies have been made. At present, people have realised that various metallic multilayers can be classified into three groups according to their atomic arrangement. The structures of these three groups are illustrated in figure 1. Figure 1(*a*) shows the case commonly designated a layered ultrathin coherent structure (LUCS) or metallic superlattice [1, 2]:

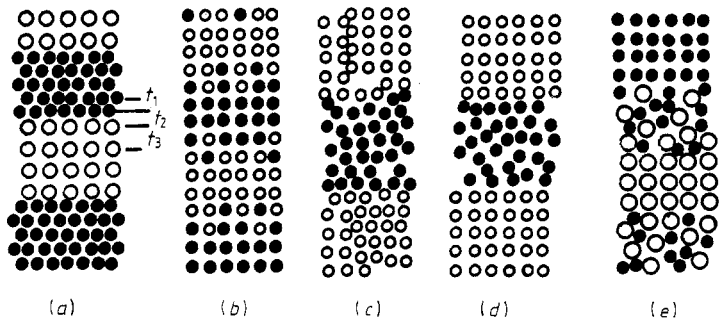

Figure 1. Illustration for the structures of various artificial metallic multilayers, (*a*) metallic superlattice, (*b*) composition-modulated multilayer, (*c*), (*d*) and (*e*) multilayered films.

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there is not only long-range coherence both in the directions perpendicular and parallel to the layers, but also a sharp interface between two constituents in these multilayers. When two constituents can mutually dissolve, the clear boundary will be replaced by an interdiffusive layer (as shown in figure 1(*b*)), these materials can be called composition modulated multilayers [3–5]. There are satellite peaks in the vicinity of the peaks corresponding to the crystal plane diffraction of components either for metallic superlattice or composition-modulated multilayer. In figure 1(*c*), (*d*), (*e*), if one or two constituents, or the boundary layer, are amorphous, the high-angle satellite peaks will be absent. The reason why the satellite peaks disappear in those cases has been studied by Clemens and Gay [6] recently. In this paper we present an x-ray diffraction and computer-simulation study on Cu–Ti artificial metallic multilayers; our results show the Cu–Ti samples made by magnetron sputtering technique are metallic superlattices.

2. Experiment

Samples were prepared in a dual-magnetron sputter deposition system with a base pressure below 4×10^{-6} Torr: the sputter pressure was 7.5 mTorr of argon gas; pure Cu and Ti targets were sputtered individually and the sample substrate was rotated over each target during the process. The relationship between the sputtering power and the deposition rate for each sputtering target was measured before preparing the samples, so that we could control the thickness ratio of two metals and modulation wavelengths in sample by adjusting sputtering power and varying the speed of substrate rotation. Actually, the same deposition rate (2.0 nm s^{-1}) for Cu and Ti targets was chosen to give equal thickness of the two metals in the samples: four kinds of samples were prepared; the modulation wavelengths were designed for 2.0 nm, 5.0 nm, 10.0 nm and 20.0 nm respectively.

The x-ray diffraction experiments were carried out on a $D/\max rB$ x-ray diffractometer: the x-ray beam was obtained from a 12 kW rotating-anode source and fine focus (0.2×2 mm^2) working mode was preferred. The x-ray wavelength was chosen with a graphite (002) crystal monochromator and Cu Kα line was used.

The measured $\theta - 2\theta$ x-ray diffraction curves of the four Cu–Ti multilayers are given in figure 2. The two peaks located at about $2\theta = 39°$ and $2\theta = 43°$ are the FCC Cu 111 peak and the HCP Ti 002 peak. Comparing the lattice parameters for Cu and Ti derived from these peaks with those for pure materials, the differences are less than 1%. Because the peaks other than Cu 111 and Ti 002 peaks do not appear on the x-ray diffraction patterns, it can be concluded that Cu and Ti grow alternately in the [111] direction and [002] direction, or at least, in these samples the copper and titanium are polycrystalline with very strong [111] and [002] texture respectively. The modulation wavelengths of multilayers can be derived from the peaks in the small-angle region, as well as from the peaks in the high-angle region. The relationship between the position of the small-angle peak and the modulation wavelength is the Bragg equation $2d \sin \theta = n\lambda$, and the positions of the high-angle peaks obey $2d(\sin \theta_i - \sin \theta_{i-1}) = \lambda$, [7], where λ is the wavelength of Cu Kα line, d is the modulation wavelength of the multilayer, θ_i and $\theta_i - 1$ are the positions of two adjacent diffraction peaks (including central peaks and satellite peaks). For sample 1 (figure 2(*a*)), the modulation wavelength derived from the small-angle peak is 1.82 nm. For sample 2 (figure 2(*b*)) the modulation wavelengths derived from several small-angle peaks and from several pairs of high-angle peaks have the

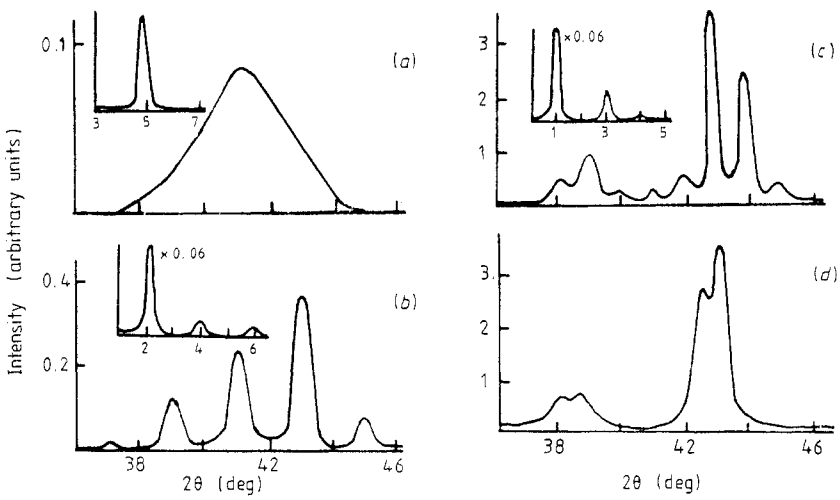

Figure 2. X-ray θ–2θ scans of Cu–Ti multilayers with modulation wavelength of (*a*) 1.82 nm, (*b*) 4.56 nm, (*c*) 9.2 nm, (*d*) 20.1 nm.

same average value $d = 4.56$ nm. For sample 3 (figure 2(*c*)), however, the modulation wavelength derived from the first small-angle peak is obviously shorter than the values derived from the second and the third small-angle peaks. The reason for this phenomenon can be explained by refractive error [8]: when the diffraction angle is small enough, correction of the refractive index becomes necessary. The average value of the modulation wavelengths derived from several pairs of high-angle peaks is 9.2 nm for this sample. For sample 4 (figure 2(*d*)), the average value of modulation wavelengths derived from two pairs of high-angle peaks is 20.1 nm. Comparing the actual values with the designed values, the errors are not more than 10%.

It deserves to be mentioned that there is an obvious even-extinction phenomenon for small-angle curves for sample 3; the second Bragg peak is much lower than the third Bragg peak.

3. Two simulation models

As shown in figure 2, there are two Cu–Ti samples that exhibit clearly quite a number of high-angle satellite peaks, therefore these samples do not belong to the multilayers of the third group mentioned above: we have only used two simulation models that are suitable for the metallic superlattice and the composition-modulated multilayer respectively. For the metallic superlattice, the one-dimensional simulation model proposed by Shuller [1] was used. In this model, the distance between the atomic planes is given by the corresponding distances of the pure metals, except for the closest plane to the interface (t_1 and t_3) and the separation (t_2) between dissimilar atomic planes. t_1, t_2 and t_3 are adjustable parameters that can be determined in fitting calculations. In addition, we have introduced two groups of random numbers which obey Gaussian distribution to simulate the fluctuations of the Cu atomic plane number and the Ti atomic plane number in every period, because layer-thickness fluctuations are impossible to

avoid in the fabrication of artificial multilayers. The degree of the fluctuation can be expressed by the root-mean-square

$$S_i = \left[\sum_{j=1}^{N} (n_j^i d^i - n_0^i d^i)^2 / N\right]^{1/2} \tag{1}$$

where i represents Cu or Ti, S is the root-mean-square factor of the Cu or Ti layer, d the distance between the atomic planes, n_j the number of atomic planes in the jth period, n_0 the average number, and N the total number of periods. We can obtain the degree of the layer-thickness fluctuation by adjusting the root-mean-square S_i in the calculation. The structure factor of the jth period is

$$F_j(\theta) = \sum_{k=1}^{m_j} \rho_k f_k(\theta) \exp\left[\mathrm{i}\frac{4\pi \sin\theta}{\lambda} z_k - B_k\left(\frac{\sin\theta}{\lambda}\right)^2\right] \tag{2}$$

where $m_j = n_j^1 + n_j^2$ is the total number of Cu and Ti atomic planes in the jth period, z_k and ρ_k the position and the plane density of the kth atomic plane respectively, $f_k(\theta)$ the scattering factor of the atoms, and B_k the Debye–Waller coefficient, which varies for each constituent. The x-ray intensity is given by [9]

$$I(\theta) \propto \frac{1 + \cos^2 2\theta}{\sin 2\theta} \sum_{k=1}^{M} \left|\sum_{j=1}^{L} F_j(\theta)\right|^2 \tag{3}$$

where M is the integer part of N/L, L is the coherence-length factor (multiply L by wavelength is the coherence length). Since the structural coherence length is limited, L may be smaller than N, we can also estimate the coherence length by adjusting L in the calculation.

On the other hand, for composition-modulated multilayers there are interdiffusive layers; the thickness of these layers (t) is adopted as an adjustable parameter in fitting calculation. Assuming that the composition change is linear in interdiffusive layers, the contribution of these layers to the structure factor of this period can be approximately given by

$$F_j(\theta) = \exp\left[-B\left(\frac{\sin\theta}{\lambda}\right)^2\right] \int_z^{z+t} f\rho \exp\left(\mathrm{i}\frac{4\pi \sin\theta}{\lambda} x\right) \mathrm{d}x \tag{4}$$

$$f\rho = f_1\rho_1 + \frac{z - x}{t}(f_1\rho_1 - f_2\rho_2). \tag{5}$$

In (4), B is the average value of Debye–Waller coefficients of Cu and Ti, z and $z + t$ the positions of the interdiffusive layer. In (5), when the layer is the Ti transition from Cu, f_1 and ρ_1 are the scattering factor and the density of the Cu atomic plane respectively, f_2 and ρ_2 are those of the Ti atomic plane respectively; when the layer is the Cu transition from Ti, the meaning of f_1, ρ_1 and f_2, ρ_2 are mutually exchanged. In order to determine the structure accurately, the structure-parameter number should be not more than the experimentally measured peaks [10], so that only sample 2 and sample 3 experimental data were taken in the following analyses, these two samples have enough diffraction peaks. The calculation were made on IBM personal computer, FORTRAN language was used. The random numbers were produced by computer; the atomic scattering factors, absorption coefficients and Debye–Waller coefficients were found in references [11], [12] and [13] respectively.

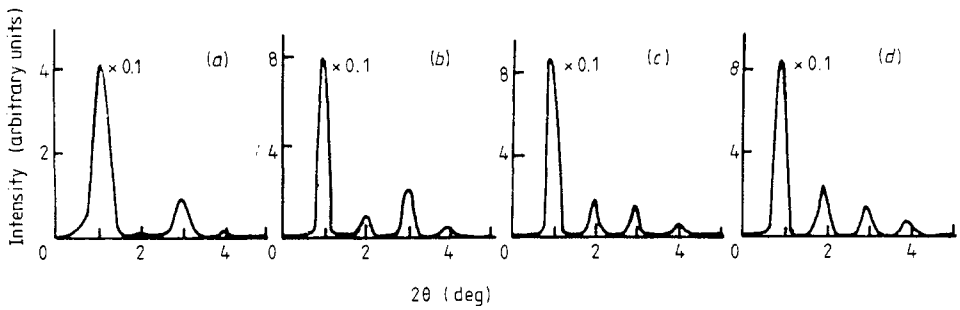

Figure 3. A comparison of (*a*) measured and (*b*), (*c*), (*d*), calculated patterns of Cu–Ti metallic multilayer with modulation wavelength of 9.2 nm. (*b*) two atomic planes, (*c*) four atomic planes, (*d*) eight atomic planes.

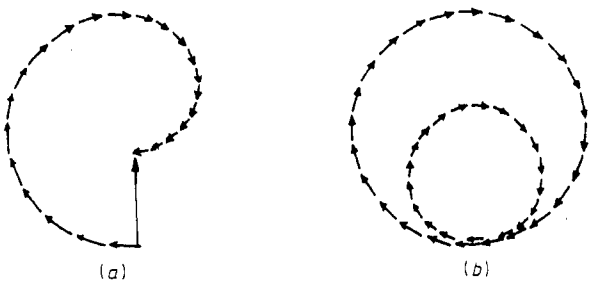

Figure 4. Illustration for phase angle and amplitude of atomic planes' diffraction vectors in a period on first (*a*) and second (*b*) Bragg conditions.

4. Results and discussion

Both the metallic superlattice and the composition-modulated multilayer simulation models can give x-ray diffraction patterns similar to the measured curves in the high-angle region by adjusting the adjustable parameters. However, the best fitting patterns in the small-angle region and the high-angle region require different structure parameters, according to the composition-modulated multilayer model. In the high-angle region, the thickness ratio tends to deviate from 1 : 1, but in the small-angle region, this thickness ratio tends to equal 1 : 1. If we let the thickness ratio deviate from 1 : 1 in the small-angle region, the thickness of the boundary layer tends to zero. And what is more, even when the thickness ratio is assumed to be 1 : 1, the calculated curves are not very well satisfied. A comparison of the calculated curves with the measured curves for sample 3 is shown in figure 3. It can be seen that the thinner the interdiffusive layers, the lower the second Bragg peaks, but the second Bragg peak is higher still, even for the thinnest interdiffusive layers (two atomic planes). If we further reduce the thicknesses of interdiffusive layers, the composition-modulated multilayer model will become the metallic superlattice model; therefore it seems that the structure of the Cu–Ti sample belongs to the metallic superlattice rather than composition-modulated multilayer. The reason for even extinction phenomenon for the metallic superlattice is illustrated in figure 4. For the condition of the second Bragg diffraction, the diffraction vectors of the first atomic plane and the

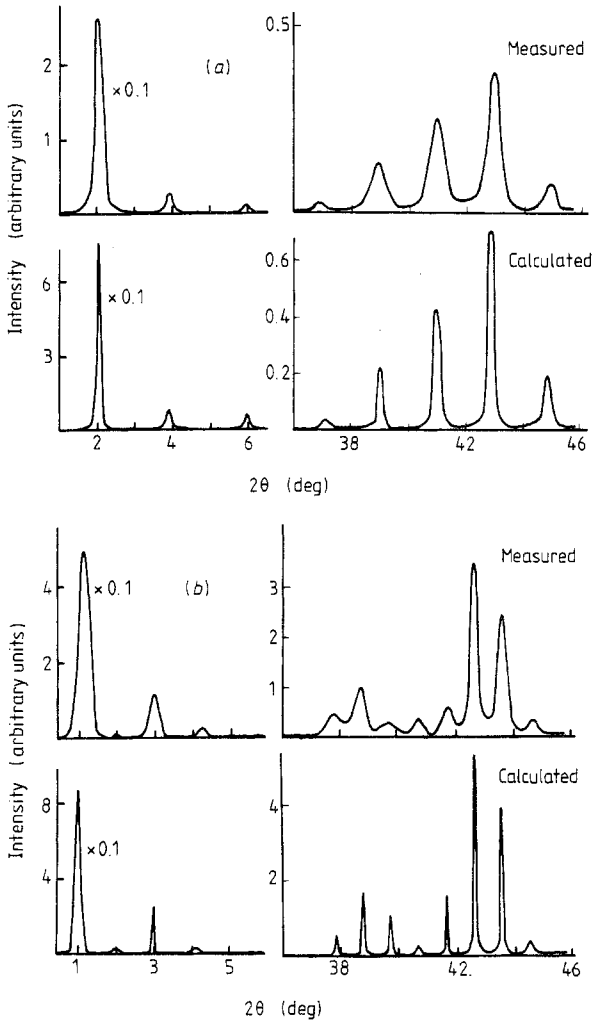

Figure 5. Measured and calculated x-ray θ–2θ scans; the modulation wavelengths are (*a*) 4.56 nm and (*b*) 9.2 nm.

last atomic plane of one component in a period have the same phase angle; all diffraction vectors of one component compose a closed circle, so that the total vector equals zero. On the other hand, the phenomenon of even extinction is evidence that the Cu–Ti samples are metallic superlattices.

The best fits with the superlattice model are shown in figure 5. Compared with experimental data, the differences of the peak positons of the calculated curves are all within 0.15° (2θ) and the differences of the peak intensities less than 8%. The results of the fits are summarised in table 1. We have found in the fitting calculation that the relationships between the parameters t_1, t_2, t_3 and the positions and intensities of the high-angle satellite peaks are very close. The thickness ratios, however, have a strong effect on the intensity ratios of the Cu and Ti structure lines, as well as on the intensity ratios of small-angle peaks. Both the root-mean-square and the coherence length influence the peak intensities and peak widths, but their effects are somewhat different, the

Table 1. The structure parameters of Cu–Ti metallic superlattices.

Wavelength (nm)					Thickness ratio		S (nm)		
Designed	Measured	t_1 (nm)	t_2 (nm)	t_3 (nm)	Designed	Measured	Cu	Ti	Coherence length (nm)
5.0	4.56	0.196	0.219	0.231	1:1	1:1.19	0.14	0.18	50.0
10.0	9.2	0.196	0.219	0.230	1:1	1:1.11	0.20	0.20	200.0

former affects the high-order Bragg peaks and the satellite peaks more strongly; the latter, however, is almost independent of diffraction orders.

In table 1, the t_1, t_2, t_3 parameters of two Cu–Ti samples that have different wavelengths are nearly identical; this result indicates that the interface structures of the two samples are the same. The values of t_1, t_2, t_3 show that the distances between the closest plane to the interface (t_1 and t_3) are shorter than the corresponding distances of the Cu(111) and the Ti(002) planes (0.209 nm and 0.234 nm); the distance between the Cu and Ti atomic planes at the interface (t_2) is nearly equal to the average value of the Cu(111) and Ti(002) planes. A notable difference between two samples is the coherence lengths; the value for sample 2 is 50 nm, that for the other one is 200 nm. There may be two reasons for the shorter coherence length of sample 2; one is that the interface number of sample 2 is more than that of the other one, because the modulation wavelength is shorter in this sample. It is clear that the structure coherence is easily lost at the interface. Another reason could be that the thickness fluctuation is more serious in this sample, the degree of fluctuation is about 8%; however, that of the other one is only about 4%.

Comparing the x-ray diffraction behaviours and the structure parameters obtained from the fitting calculation with those of Nb–Cu systems [2, 10, 14], it is worth mentioning that the quality of the Cu–Ti superlattices is better than that of the Nb–Cu superlattices. The reason for the better quality can be explained by the match condition of the mating atomic planes at the interface, because for the Cu(111) and Ti(002) planes, the two mating atomic planes in Cu–Ti superlattice have the same structure (hexagonal close-packed plane), while for the Nb(110) and Cu(111) planes, the two mating atomic planes in Nb–Cu superlattice have different structure, and comparing the lattice-mismatch degrees with each other, it can also be found that the lattice-mismatch degree of the Cu(111) and Ti(002) planes is smaller than that of Nb(110) and Cu(111) planes.

In addition, we have used EXAFS technique to study the interface structure of Cu–Ti superlattice, the EXAFS results prove that the atomic arrangement at the interface is quite orderly. The details of this work have been reported elsewhere [15].

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