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Grazing incidence x-ray scattering study of the structure of epitaxial Cr/Sn multilayers

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The structure of epitaxial Cr/Sn multilayers has been studied experimentally using x-ray reflectivity and x-ray diffuse scattering measurements, as well as theoretically using linear muffin-tin orbital (LMTO) calculations. Measurements show a distinct variation in the structure of the multilayers as the Sn layer thickness increases from 0.4 to 0.6 nm. A decrease in the electron density of the Sn layer and an increase in the jaggedness of the interfaces accompany a partial transformation of the Sn layer from an epitaxial bcc structure to a β-Sn structure, as observed using in situ reflection high energy electron diffraction measurements [K. Mibu, S. Tanaka, and T. Shinjo, J. Phys. Soc. Jpn. 67, 2633 (1998)]. Present measurements along with the LMTO calculations support a structure for the multilayer in which Sn layers grow epitaxially with Cr in a bcc structure with a finite density of steps at the interfaces which causes the average electron density of a Sn layer to decrease. Diffuse scattering measurements give the average distance between steps to be about 50–100 nm. Taking the structure of the epitaxial Sn layer to be bcc, the calculated variation in the lattice strain and Sn layer energy with the thickness of Cr and Sn layers explains qualitatively the range of Cr layer thicknesses for which epitaxial growth is observed. © 2001 American Institute of Physics.

[I. INTRODUCTION]

Several studies on the magnetism of thin Cr films have been reported in recent literature.1–4 Magnetism of thin Cr films is crucial in understanding the giant magnetoresistance in multilayer systems like Fe/Cr. Among a variety of techniques used to study this system, recently, Mibu et al. have successfully used Mössbauer spectroscopy to probe the magnetism of a Cr layer by introducing a thin layer of Sn, which itself is nonmagnetic, as a Mössbauer probe.2,3 Success of the technique stems from the fact that it has been possible to grow a Sn layer epitaxially with Cr. Thus the probe layer affects insignificantly the structure as well as the magnetism of the Cr layer. Epitaxial multilayers of Cr/Sn with subnанometer thick Sn layers have been grown on MgO(001) substrate.2,4 Reflection high energy electron diffraction (RHEED) measurements during the growth showed that the Cr layers grow with the structural relation MgO[100]/Cr[110] in the film plane, and that the Sn layers have structural coherency with the Cr layers. High resolution x-ray diffraction (XRD) measurements also show satellites around the (002) peak of Cr, indicating the epitaxial nature of the multilayers.2 With increasing thickness of the Sn layer, Sn grows epitaxially with Cr up to a thickness of 0.5 nm, beyond which β-Sn begins to grow in an island growth mode. On the other hand, for a fixed Sn layer thickness of one monolayer, the epitaxial multilayer structure is found to grow down to a Cr layer thickness of about 0.6 nm. The q-space mapping around the Cr(112) peak shows that the in-plane lattice parameter of the multilayer is somewhat larger than that of the bulk chromium. It has been suggested that Sn grows epitaxially with a bcc structure, Sn atoms at the interface occupying the body center points of the underlying Cr layer.

The aim of the present work is to further elucidate the structure of epitaxial Cr/Sn multilayers using x-ray reflectivity and diffuse scattering measurements. X-ray specular reflectivity provides information about the electron density of different layers and thus can yield information about the structure of the Sn layer. X-ray diffused scattering along with reflectivity measurements also provides detailed information about the structure of interfaces between Cr and Sn layers. Linear muffin-tin orbital (LMTO) calculations have also been done, and the results compared with some of the experimental findings in order to confirm the structure of the Cr/Sn superlattice.

II. EXPERIMENTAL TECHNIQUE

The multilayers studied in the present work are the same as used in Ref. 2. Samples were prepared by alternate deposition of Cr and Sn layers on MgO(001) substrates kept at 200 °C in a vacuum of 10−9 Torr. The epitaxial nature of the films was confirmed from the streak pattern in in situ RHEED measurements as well as from the satellite peaks around the high angle x-ray diffraction lines.2 Three multilayers having structure MgO(001)/[Cr(5.0 nm)/Sn(t nm)] × 10 with t = 0.2, 0.4, and 0.6 nm (designated as S2, S4, and S6) were studied.
X-ray reflectivity as well as diffuse scattering measurements were done using a Siemens D5000 diffractometer with Cu Kα radiation. Measurements were done in specular geometry (with angle of incidence θi equal to the angle of reflection θr), as well as in off-specular geometry with an offset of Δθ=0.05° between θi and θr. Rocking curve measurements show that at an offset of 0.05° the specularly reflected component is almost completely removed. Thus in an offset scan one measures the diffuse scattering as a function of the normal component of the momentum transfer vector qz. True specular reflectivity is obtained by subtracting the off-specularly reflected intensity from the specular one. Diffuse scattering as a function of the in-plane component of the momentum transfer vector qx was measured by keeping the scattering angle 2θ fixed and rocking the specimen around θi=θr.

III. LMTO CALCULATIONS

Theoretical calculations were done to determine the equilibrium structure of a Cr/Sn multilayer with tin growing epitaxially with bcc structure. Self-consistent supercell energy band calculations were done using tight binding linear muffin-tin orbital formalism within atomic sphere approximation (ASA).5 Spin averaged calculations were performed using the Volko–Wilk–Nusair local density exchange correlation potential. The actual multilayer system has been modelled by a (m+n) supercell with m layers of Cr and n layers of Sn periodically repeated along the [001] direction which is the growth direction. Starting from (1+1) supercell calculation, we have gone to (15+7) supercell by increasing the number of Cr and Sn layers. In these calculations both Cr and Sn layers have been considered to have bcc structure and the supercell has tetragonal structure. All the calculations are semirelativistic and with frozen core approximation. Since the supercells here are closely packed, the atomic sphere overlaps (<16%) are well within the permissible limit of ASA. The supercell calculations are done using 8k points each along the x and y direction (in-plane), 2k points along the z direction (growth direction), and 30k points in the irreducible Brillouin zone. The Brillouin zone integration in the k space is performed by means of the tetrahedron method. Two sets of calculations were done. In one set, the thickness of the Sn layer was kept constant at one monolayer, while varying the thickness of the Cr layer from 15 to 1 monolayer. The calculation for bulk Cr has also been done by the usual method. The in-plane equilibrium lattice constants were determined by minimizing the total energy of the supercell, keeping the out-of-plane lattice constant fixed at experimental value (the lattice spacing between Cr atomic layers is 0.144±0.001 nm, and that between Sn layers is 0.170±0.008 nm). The obtained variation of the equilibrium lattice constant for different thicknesses of the Cr layers is shown in Fig. 1(a). In the second set, the in-plane lattice constant was also kept fixed at 0.288 nm, and the energy per Sn atom in the Sn layer was obtained as a function of Cr layer thickness. The results are shown in Fig. 1(b).

IV. RESULTS

Figure 2 gives the true specular reflectivity as well as off specular reflectivity of the three specimens. In specimens S4 and S6 the Bragg peaks due to the periodicity of the multi-

![Graph of Equilibrium Lattice Constant and Total Energy](image)

**FIG. 1.** (a) Equilibrium lattice constant (dotted line) for Cr/Sn where n gives the number of monolayers. n=500 gives the results for bulk Cr. (b) Total energy on the Sn layer (broken line) for Cr/Sn multilayers for a fixed lattice constant of 0.288 nm.

**FIG. 2.** The true x-ray specular reflectivity and off-specular reflectivity scans (dotted curves) of [Cr(5.0 nm)/Sn(3 nm)]x10 multilayers on MgO[001] substrates with different values of thickness t, of Sn layers designated as S2, S4, and S6. The true reflectivity is obtained by subtracting the off-specularly reflected intensity from the specular data. Theoretical fits to the specular reflectivity data are also shown (continuous curve).
layers are clearly visible in the range of $\theta>0.7^\circ$. Bilayer periodicity as obtained from the position of the Bragg peak agrees very well with the designated periodicity. In specimen S2, because of the small Sn layer thickness, the x-ray contrast is too small to give appreciable intensity of the Bragg peak.

A detailed analysis of the reflectivity pattern can yield valuable information about the electron density in various layers and the rms roughness of interfaces. The true specular reflectivity patterns were fitted using Parratt’s formalism\(^6\) with the following constraints: (i) the rms roughnesses of different interfaces were taken to be equal and as a fitting variable, (ii) electron density and hence the refractive index of the chromium layer was taken to be equal to the bulk value, while that of Sn was taken as a fitting variable. The results of the fitting of the experimental data are shown in Table I. In order to demonstrate how sensitively the reflectivity pattern depends upon the electron density in the Sn layer, in Fig. 3 is shown the simulated reflectivity patterns for specimens S2 and S4 for different values of Sn layer electron density. Perusal of Table I shows that in specimens S2 and S4 the electron density of the Sn layer is substantially greater than that for bulk Sn, while in S6 the value is close to that of bulk Sn. The result is interesting because generally in polycrystalline films the electron density is less than that in the bulk, due to a large density of imperfections in the as-deposited film. The electron density of the Sn layer would depend upon the number of Sn atoms per unit volume and hence upon the structure of this layer. Therefore the observed electron density of this layer in the present case can be used to deduce its structure.

In all three specimens, the off-specular reflectivity replicates some of the features of specular reflectivity: while in S2 the total thickness oscillations are clearly visible in the range of $\theta>0.7^\circ$, in S4 and S6 only faint Bragg peaks are visible. It has been suggested that the presence of total thickness oscillations in off-specular reflectivity signifies a high degree of correlation of the interface structure from layer to layer.\(^7\)\(^8\) Thus in the specimen S2 the interface structure of successive layers is highly correlated, while in specimens S4 and S6 the interface correlation is only partial.

The diffuse scattering measurement provides information about the structure of the interfaces in the film plane. The in-plane structure of the interfaces can be described in terms of a height–height correlation function, $c(x,y)$, which in most of cases can be written as

$$c(x,y) = \sigma^2 \exp(-|R|/\xi)^{2h},$$

where $\xi$ is the in-plane correlation length of the interface height variation and $h$ is the fractal dimension which takes care of jaggedness of the interface. In a multilayer structure, in general, a part of the interface height variation is correlated between successive layers, while another part is uncorrelated, the two components in general having different in-plane correlation lengths, $\xi_c$ and $\xi_u$, respectively. In order to get separate information about $\xi_c$ and $\xi_u$, diffuse scattering was measured at two different values of $2\theta$: one corresponding to the maximum of the first Bragg peak due to the

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$\sigma$ (nm)</th>
<th>$\delta$ ($10^{-4}$)</th>
<th>$\beta$ ($10^{-6}$)</th>
<th>Electron density $(10^{24} \text{e/cm}^3)$</th>
<th>$\xi_c$ (nm)</th>
<th>$\xi_u$ (nm)</th>
<th>$h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2</td>
<td>0.8±0.05</td>
<td>-25.0</td>
<td>-2.60</td>
<td>2.3433</td>
<td>150±10</td>
<td>50±10</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>S4</td>
<td>0.9</td>
<td>-25.0</td>
<td>-2.60</td>
<td>2.3433</td>
<td>150</td>
<td>100</td>
<td>0.6</td>
</tr>
<tr>
<td>S6</td>
<td>0.9</td>
<td>-19.5</td>
<td>-2.18</td>
<td>1.8278</td>
<td>150</td>
<td>100</td>
<td>0.6</td>
</tr>
</tbody>
</table>

FIG. 3. Theoretically generated x-ray reflectivity scans of [Cr(5.0 nm)/Sn(t nm)]×10 multilayers on MgO(001) substrates with $t = 0.2$ and 0.4 nm, and for different values of $\delta$ for the Sn layer. Different curves are displaced vertically relative to each other for the sake of clarity.
multilayer periodicity, and the second corresponding to the minimum in the intensity immediately following the first Bragg peak. It may be noted that for the value of $2\theta$ corresponding to the Bragg peak, diffuse scattering due to the correlated part of the roughness from successive interfaces add coherently, and therefore, the contribution of the correlated part of the roughness is proportional to $N^2$ ($N$ being the number of interfaces in the multilayer) while the contribution of the uncorrelated part of the roughness is proportional to $N$. On the other hand, for the value of $2\theta$ corresponding to a minimum in the specular reflectivity, diffuse scattering amplitudes due to the correlated part of the roughness at different interfaces interfere destructively, thus reducing its contribution to the total intensity, while the contribution of the uncorrelated parts of the roughness remains unaltered. Thus the diffuse scattering at the Bragg peak has a higher contribution from the correlated part of the roughness, while that at the adjacent minimum has a higher contribution from the uncorrelated part of the roughness. Figure 4 gives the diffuse scattering curves of the specimens S4 and S6. The data on the specimen S2 is not presented, since in this specimen, due to poor contrast between Cr and Sn layers, no reliable information can be obtained about the Cr/Sn interfaces.

The fitting of the nonspecular data are done by using the program TRDS_sl, the access to which was kindly provided by Dr. S. Stepanov of Illinois Institute of Technology, Chicago. Simulations of the scattering from multilayers with interface roughness are done using the model suggested by Ming et al., which is formulated with the assumption that vertical correlation does not depend on the lateral size of roughness. The variables used for fitting the data are the rms interface roughness $\sigma$, the fractal dimension $h$, the longitudinal correlation length $\kappa$, and the lateral correlation length $\xi$. The fitted values of the parameters are also given in Table I. Typical uncertainties in the values of $\xi$, $\kappa$, and $h$ are $\pm 10$ nm, $\pm 20$ nm, and $\pm 0.2$, respectively. It may be noted that in both the specimens, the in-plane correlation length for the vertically correlated roughness $\xi_z$ is more than that for the vertically uncorrelated part $\xi_u$. Further, on going from specimen S4 to S6, the jaggedness of the interfaces shows a distinct increase, the parameter $h$ going from 1.0 to 0.6.

V. DISCUSSONS

In the earlier studies on this system, it has been suggested that Sn atoms are located at the center of the square lattice of the Cr (001) surface, forming a bcc lattice together with the Cr atoms. Mössbauer results also agree with this picture: (i) the observed Sn Mössbauer isomer shift of 1.56 mm/s is a reasonable value for Sn atoms sandwiched by Cr atoms, and (ii) a narrow hyperfine field distribution indicates a rather uniform environment of different Sn atoms.

At the interface of the MgO (substrate)/Cr layer, the constraint of a fixed in-plane lattice constant will result in an increase in the layer energy with decreasing Cr layer thickness. This aspect is presented in Fig. 1(b), where the energy per Sn atom for a fixed in-plane lattice constant is plotted as a function of the Cr layer thickness. One may note that initially the energy of the Sn layer increases slowly with decreasing Cr layer thickness. However, it shows a rapid increase below a Cr layer thickness of 4 monolayers (~0.6 nm). This large increase in the energy of the Sn layer would destabilize the epitaxial structure. This observation agrees with the experimental fact that below a Cr layer thickness of 0.6 nm it is difficult to form an epitaxial structure. Thus present calculations indirectly support a structure for a Cr/Sn superlattice in which Sn grows epitaxially with a bcc structure.

The results of x-ray reflectivity and x-ray diffuse scattering can be used to further elucidate the structure of a Cr/Sn superlattice. If the Sn atoms take the lattice of Cr with lattice constant equal to 0.288 nm, the calculated electron density in the Sn layer comes out to be 3.4588 x 10^24 e/cm^3, which is much higher than that obtained from the fitting of specular reflectivity data in specimen S4, as given in Table I. However, it is expected that if Sn atoms take the lattice structure of Cr in the film plane, its lattice would expand along the $z$ direction, thus reducing the electron density. Experimentally, the position of the principal XRD peak around Cr (200), which gives average lattice spacing along the growth direction, can be explained by assuming that the lattice spacing between Cr atomic layers is 0.144 ± 0.001 nm, and that between Sn layers is 0.170 ± 0.008 nm. The electron density of
the Sn layer as calculated using these parameters is still substantially higher than the experimental value. From LMTO calculations for a Sn layer thickness of 0.4 nm the out-of-plane lattice spacing between the Sn layer comes out to be 0.2 nm which is even higher than the experimentally deduced value. However, even with this value, the calculated electron density is $2.977 \times 10^{24} \text{e/cm}^3$, which even now is higher than the value obtained in Table I. This discrepancy can be explained in terms of a finite step density at the interfaces. A finite step density will result in substitution of a fraction of Sn atoms by Cr atoms in a given layer, thus reducing the electron density of Sn layers. In the specimen S6, the fitted electron density is close to that for bulk $\beta$-Sn. However, since in this case also, a finite step density at the interfaces would reduce the effective electron density of a Sn layer, the actual electron density of the Sn layer is higher than that of bulk $\beta$-Sn. Thus in specimen S6 the electron density is higher than that in bulk $\beta$-Sn but less than that in specimens S2 and S4. This result agrees with the observations of earlier RHEED measurements, that at a Sn layer thickness of 0.6 nm $\beta$-Sn begins to grow in an island growth mode.\(^2\)

Since one expects that the position of steps will be uncorrelated from layer to layer, the steps will contribute to the uncorrelated part of the roughness. Thus the lateral correlation length $\xi_u$, as obtained from the diffuse scattering measurements at a $2\theta$ value corresponding to the reflectivity minimum, may be taken as an average distance between two steps. The correlation length $\xi_c$ on the other hand may be associated with the height variation of the substrate itself, which gets replicated at successive interfaces. Further, from diffuse scattering measurements one finds that as one goes from specimen S4 to S6, the jaggedness of the interfaces increases. This increase may be attributed to a partial transformation of the structure of the Sn layer from bcc to $\beta$-Sn in specimen S6, in conformity with the results of RHEED measurements.\(^2\)

**VI. CONCLUSIONS**

The structure of epitaxial Cr/Sn multilayers has been studied experimentally using x-ray reflectivity and x-ray diffuse scattering measurements, as well as theoretically using LMTO calculations. X-ray reflectivity as well as x-ray diffuse scattering measurements show a distinct variation in the structure of the multilayers as the Sn layer thickness increases from 0.4 to 0.6 nm. A decrease in the electron density of the Sn layer and an increase in the jaggedness of the interfaces signals a partial transformation of the Sn layer from an epitaxial bcc structure to a $\beta$-Sn structure, in confirmation with the results of in situ RHEED measurements.\(^2\)

Present measurements support a structure for the multilayer in which Sn layers grow epitaxially with Cr with a finite density of steps at the interfaces. Diffuse scattering measurements give the average distance between steps to be about 50–100 nm.

Taking the structure of an epitaxial Sn layer to be bcc, the calculated variation in the lattice strain and Sn layer energy with the thickness of Cr and Sn layers explains qualitatively the range of Cr layer thicknesses for which epitaxial growth is observed.