Quantitative characterization of epitaxial superlattices by x-ray diffraction and high resolution electron microscopy

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Quantitative x-ray diffraction (XRD) and high resolution electron microscopy (HREM) have been applied to the analysis of an epitaxial CoO/NiO superlattice. This example shows that the qualitative information determined directly from a XRD spectrum or HREM image is limited and can even be misleading. However, by a combination of quantitative intensity measurements and structural modeling, a detailed quantitative characterization of the superlattice structure is possible.

Quantitative structural determination is of the utmost importance in understanding many of the anomalous physical properties observed in superlattices.[1] Structural properties of interest include epitaxial orientations, lattice strains, layer thickness fluctuations, interface coherency, and interdiffusion. These structural properties will strongly depend on both the particular superlattice system studied and the growth method. X-ray diffraction (XRD)[2] and high resolution electron microscopy (HREM)[3,4] are the two techniques most commonly used to characterize superlattices.

XRD measures scattered intensities, so the phase information is lost. Because of this, it is impossible to directly deconvolute measured intensities to obtain the structure. While HREM images result from phase contrast, unique structure determination from images is impractical. Additionally, both techniques give average measurements of the superlattice: XRD averages over the illuminated area of the sample and HREM averages over the path length of the electron through the sample. Therefore, modeling of the structure is required to compare with the measured intensities to quantitatively determine the structure. Particularly in HREM, the images obtained can give ambiguous or misleading results when they are not compared with model calculations because of the sensitivity to specimen thickness and microscope parameters (notably defocus). As an example, we present detailed XRD and HREM studies on an epitaxial CoO/NiO superlattice.

For this study a [CoO(23 Å)/NiO(23 Å)]$_{15}$ superlattice was grown epitaxially on a (0001) α-Al$_2$O$_3$ substrate by reactive sputtering. The deposition conditions and epitaxial relationships of the monoxide films are discussed elsewhere.[5,6] The XRD spectra were taken on a 12 kW Rigaku rotating anode x-ray diffractometer using Cu K_α radiation. The HREM images of sample cross sections were taken on the JEOL ARM-1000 at the National Center for Electron Microscopy (NCEM) at Berkeley, CA.

Bulk CoO and NiO share the NaCl structure with lattice constants 4.260 and 4.1769 Å, respectively. Epitaxial thin films of CoO and NiO grown under identical conditions as the superlattice were oriented (111) with lattice spacings 2.460 and 2.423 Å, respectively.[5,6] While this is essentially the bulk CoO value, the NiO is expanded 0.5% over the bulk value. Figure 1(a) shows the measured high-angle x-ray diffraction spectrum of the CoO/NiO superlattice. The main diffraction peak located at 36.69° (2.449 Å), intermediate between the CoO(111) and NiO(111) positions, confirming the (111) orientation of the superlattice. The average lattice spacing, determined from the main peak position, is expanded $\approx 0.3\%$ over the expected value, 2.441 Å, calculated from the thin-film values. Finite size peaks about the main diffraction peak in the measured spectrum shows that crystalline coherence is maintained over the total thickness of the superlattice (690 Å). The full width at half maximum of a high-angle θ scans is 0.08° indicating a high degree of orientation.

Because the peak positions depend only on the average lattice spacing and modulation wavelength, Λ, structural information about the constituent layers requires comparing the calculated diffraction intensities of a structural model with the measured intensities. By adjusting the structural parameters of the model to best fit the measured intensities, the structure of the layers can be quantitatively refined.[7,8] The best-fit is given by the solid line in Fig. 1(a). The model includes the average layer thicknesses, lattice spacings of the CoO and NiO layers including strain profiles near each interface,[7,8] and two disorder mechanisms: (i) discrete atomic layer thickness variations and (ii) continuous Gaussian fluctuations of interface lattice spacings.[7-11]

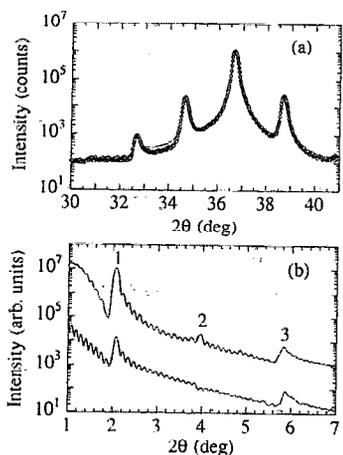From the fit, the average thicknesses of the layers are 9.3±0.5 monolayers of CoO and 9.5±0.5 monolayers of

FIG. 1. X-ray diffraction spectra of [CoO(23 Å)/NiO(23 Å)]$_{15}$ super-lattice. (a) Measured (circles) and refined (line) high-angle spectra. The refined spectrum includes $K_{\alpha 1}$-$K_{\alpha 2}$ splitting and instrumental line broadening of 0.05° 2θ. (b) Measured (upper curve) and calculated (lower curve) low-angle spectra.

FIG. 2. HREM images of a [CoO(23 Å)/(NiO(23 Å)]$_{15}$ superlattice, (a) low magnification and (b) high magnification. Arrows indicate strain fields in CoO layers. C and N refer to CoO and NiO layers, respectively.

NiO in agreement with the growth parameters. The constituent layers are smooth with discrete layer thickness fluctuations limited to one monolayers steps about the average. The width of the continuous interface fluctuations is 0.04 Å indicating highly coherent interfaces. The refined average lattice spacing in the growth direction of the CoO and NiO layers are 2.48±0.01 and 2.42±0.01 Å, respectively. The CoO value represents an 0.8% expansion over the thin-film value and the NiO value equals the thin-film value but is expanded over the bulk value. The lattice spacing of the NiO layer is found to be uniform throughout the layer thickness. In contrast, the best-fit for the CoO layer found the center of the layer expanded (lattice spacing ≈2.50 Å) with a contraction towards each interface to ≈2.45 Å.

Figure 1(b) shows the measured low angle diffraction spectrum for the CoO/NiO superlattice compared to the simulated spectrum[7,12] based on the structural parameters determined in the high-angle refinement. Since the x-ray scattering powers of Co and Ni are similar, the simulation includes the anomalous corrections $\Delta f'$ and $\Delta f''$.[13] The first three superlattice peaks and the higher frequency finite size peaks, which result from interference of x-ray reflections from the surface and the film-substrate interface, are clearly observed. The suppression of the second-order superlattice peak clearly shows the CoO and NiO layers are equal thickness with a square compositional profile. The broadening of the third-order superlattice peak indicates that there are some cumulative layer thickness fluctuations. The simulated spectrum assuming one monolayer steps in the layer thickness is in very good agreement with the measured spectrum in both the shape of the third-order superlattice peak and the extent of the finite size peaks.

HREM is a complimentary technique to XRD since it studies the local structure of the superlattice and is more sensitive to short-range in-plane structure. Figures 2(a) and 2(b) show a low and high magnification HREM image of the same CoO/NiO superlattice along the [110] zone
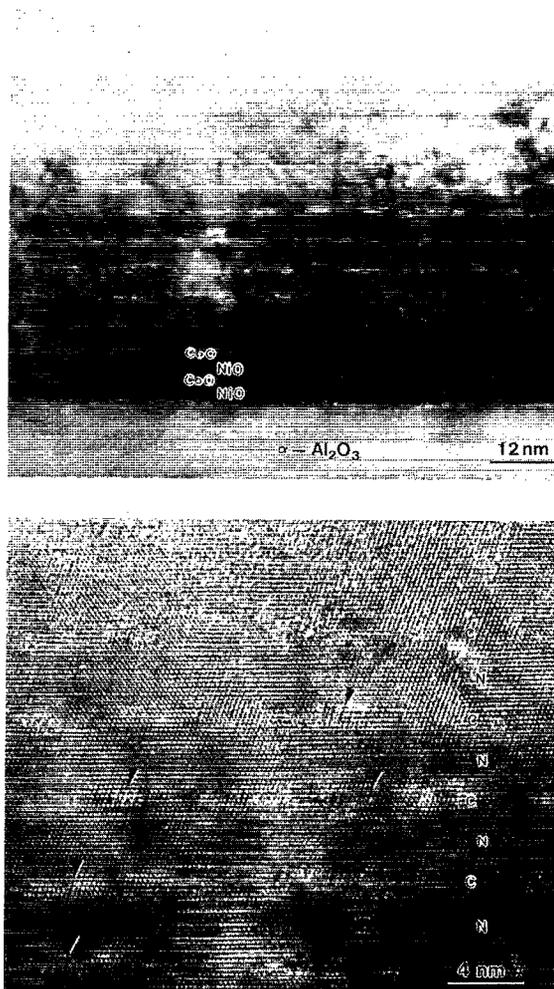
axis. The atomic resolution confirms the single-crystal nature of the superlattice and the same epitaxial orientation as the monoxide films.[5,6] A layered contrast with the superlattice periodicity is observed with the lighter contrast regions within the CoO layers. The layered contrast in the HREM suggests *unequal* layer thicknesses (the darker NiO layer being much thicker than the CoO layer) in contradiction with the growth parameters and x-ray analysis. The images also show no clear evidence of the CoO-NiO interfaces. The origin of the contrast is clearer in the higher magnification image shown in Fig. 2(b) where the arrows indicate strain fields within the CoO layers. Clearly, full interpretation of the experimental HREM images requires comparison with simulated images which contain the experimental and instrumental parameters.

Figures 3(a)–3(c) show a series of simulated images along the [110] zone axis.[14] Figure 3(a) shows simulated images assuming that the NiO and CoO have the same lattice spacing. No contrast is observed in the simulations, indicating that the contrast in Fig. 2 is not due to the contrast in scattering amplitudes of Co^{2+} and Ni^{2+} but results from structural contrast between the layers. Figure
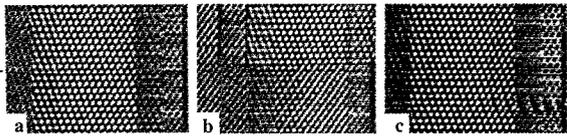
FIG. 3. Simulated HREM images of CoO/NiO bilayer for various focusing conditions and 60 Å sample thicknesses. Arrow indicates interface position. The CoO layer is below the interface and NiO above. (a) NiO and CoO layers have the same lattice spacing, (b) NiO and CoO layers have bulk lattice spacing, and (c) strain profile in the CoO layer.

3(b) shows simulated images assuming the CoO and NiO layers have their respective bulk lattice spacings. A distinct contrast change is observed at the CoO-NiO interface and equal layer thicknesses appear in the images. Figure 3(c) shows some of the simulated images in which a 3% strain profile was added to the center of the CoO layer and the NiO layer having a uniform lattice spacing. In this configuration, for appropriate defocus conditions, a contrast is observed in the center of the CoO layer resulting from the strain profile and no contrast at the interface. This agrees with all the observed images and the x-ray refinement results.

Both the XRD and HREM images are consistent with the NiO and CoO forming a coherent interface but with inhomogeneous strains in the CoO layer. Neither of these conclusions are possible without comparisons with model calculations. The origin of the different strain profiles observed for the NiO and CoO layer most likely results from the nonequilibrium growth conditions. We have found from the growth of monoxide films, that the CoO films are sensitive to the growth parameter, with impurity phases (Co_3O_4) more readily formed.[15] In contrast, the NiO structure appears very stable, with no evidence of impurity phases as long as sufficient O_2 is present during growth. This increased stability may explain why the NiO layers are similar to the thin-film structure and the CoO layer accommodates more of the lattice mismatch.

In conclusion, quantitative x-ray diffraction and high resolution electron microscopy have been applied to the analysis of an epitaxial CoO/NiO superlattice and show that the information which can be determined directly from an XRD spectrum or HREM image is limited and can even be misleading. In particular, determination of the interface position and relative layer thicknesses from HREM images may be misleading. However, by a combination of quantitative intensity measurements and structural modeling, a detailed quantitative characterization of the superlattice structure is possible. The structural information obtained by these techniques are often complimentary and when combined, can provide a complete structural characterization. It is emphasized in general, that since HREM images are so sensitive to the specimen and instrumental conditions that interpretation without simulations would be meaningless.

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