Surface Phonon Scattering in the Electrical Resistivity on Co/Ni Superlattices

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The effect of surface phonon scattering on the electrical resistivity has been observed in Co/Ni superlattices, with reproducible film microstructure, independent of the film thickness. The temperature-dependent part of the resistivity increases rapidly with decreasing film thickness for films thinner than the electronic mean free path. The resistivity shows a universal behavior well characterized by the Bloch-Grüneisen model. The deviation from the bulk resistivity can be explained by a reduced surface Debye temperature and additional surface phonon modes. [S0031-9007(96)02093-5]

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Many interesting phenomena are induced by surface boundaries of solids, such as surface states [1], surface plasmons [2], or surface phonons [3]. In thin films the size reduction in the direction perpendicular to the film surface allows the observation of many effects due to confinement of electronic states between the substrate-film and vacuum-film interfaces, such as quantum well states [4], classical size effects [5], and quantum size effects in the electrical resistivity [6]. Although these effects are generally somewhat insensitive to film microstructure, many theoretical models of the size effect have to rely on phenomenological parameters to account for structural changes with thickness [7]. In general, thin films undergo gradual structural transformations with thickness, such as lattice strains, point defects, dislocations, etc. These in turn have a strong effect on the transport properties of thin films. For this reason there have been few studies on the effect of the surface phonons on the transport properties, although the thermal conductivity of dielectric materials [8,9] and the electrical resistivity of thin films [10] are known to be sensitive to surface conditions. A temperature-dependent size effect in the electrical resistivity of metals has been reported for thin wires [11], but these experiments are limited to low temperatures (<4.2 K), where many scattering processes, other than electron-phonon scattering, are known to be significant. Consequently, the electrical resistivity of thin metallic films has been studied for many decades, but surface phonon scattering has never been clearly observed experimentally. This is partly due to difficulty in achieving uniform film microstructure for ranges of thickness where such an effect is anticipated. Here we found a strong increase in the temperature-dependent resistivity for films thinner than the electronic mean free path. This effect can be explained easily by the reduced Debye temperature and the increase in the number of phonon modes due to scattering by surface phonons.

Epitaxial Co/Ni superlattices grown on sapphire substrates [12] are ideal candidates for investigating the effect of surface phonon scattering on the electrical resistivity. First, the electronic mean free path is estimated to be long enough (~ 260 Å) [13] that a wide range of thickness is available for studies without any complication due to surface contamination. Second, no structural changes with thickness have been observed by any available structural analysis techniques [13]. On the other hand, the superlattice structure of these films did not introduce any complications into electron-phonon scattering, because Co and Ni have very similar properties, including the Debye temperature, electrical resistivity, lattice parameters, and thermal conductivity. Therefore, Co/Ni superlattices are ideal systems for study of surface phonons on the electrical resistivity.

Epitaxial Co/Ni (fcc/fcc) superlattices were grown by ultrahigh vacuum (UHV) molecular beam epitaxy (MBE) along the [111] direction, on single crystal [11.0] sapphire substrates. Sample growth, structural characterization, and electrical resistivity measurement methods were similar to those presented previously [12]. A 50 Å Co buffer layer was grown at 300 °C and subsequently annealed at 550 °C for 15 min prior to superlattice deposition at a reduced substrate temperature of 150 °C. All samples had the same ratio of Co to Ni thickness (3:2) for two different superlattice periods Λ, 25 Å and 35 Å. The number of bilayers N was adjusted to make the total film thickness d. The resistivity was measured in the temperature range of 4.2 to 300 K on photolithographically patterned samples. We want to point out that no appreciable changes have been found, either in the microstructural uniformity of superlattices or in the temperature dependent part of the resistivity, caused by different Λ.

We analyzed the film microstructure *in situ,* using reflection high energy electron diffraction (RHEED). The *in situ* RHEED profile from a single Co film, with the electron beam along the [1−10] in the fcc (111) Co surface, using the same growth parameters, is shown in Fig. 1(a). These single crystalline Co films show continuous changes in the RHEED profile with increasing thickness. The [00] RHEED streak has a narrower FWHM, higher peak intensity, and less diffuse background for thicker films. For films thinner than 300 Å, film growth is more sensitive to substrate conditions. Figure 1(b) shows

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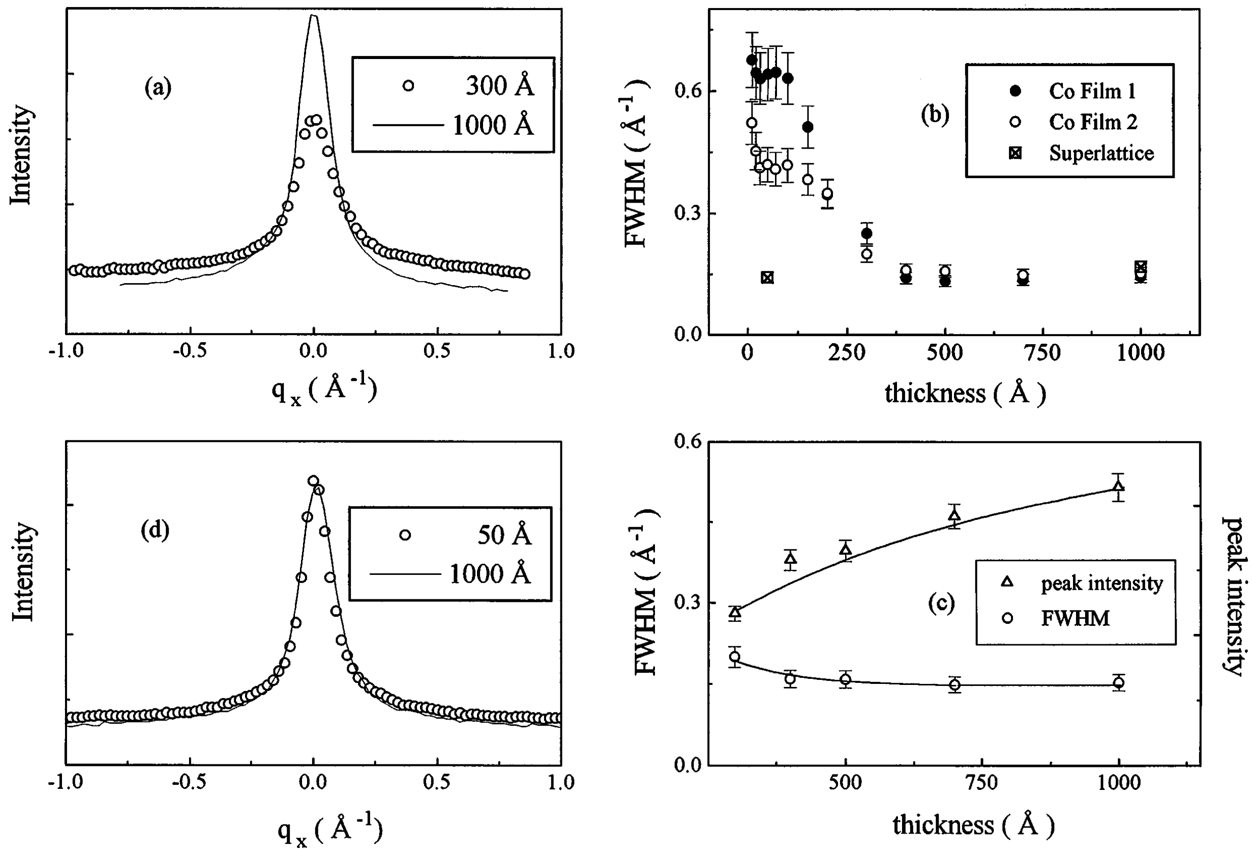

FIG. 1. (a) RHEED spot profile observed in a typical Co film. (b) FWHM of the diffraction peaks as a function of the film thickness. Co films No. 1 and No. 2 were grown on substrates prepared by slightly different procedures. Note that FWHM for 50 and 1000 Å thick *superlattices* are similar. (c) FWHM and peak intensity observed in Co film No. 2. Lines are guides to the eye. (d) RHEED spot profile observed in a typical Co/Ni superlattice film.

changes of FWHM in Co films grown on substrates subject to different Ar ion sputtering and thermal annealing procedures. Especially for films thinner than 300 Å, the film microstructure is strongly affected by the substrate preparation method, and changes dramatically with thickness. Because the effect of surface phonon scattering on transport is expected precisely in this thickness range (<300 Å), this structural change may obscure the presence of surface phonon scattering. Although for Co films thicker than 300 Å the RHEED FWHM is limited by the spatial resolution of our instrument, the increased diffraction peak intensity [Fig. 1(c)] suggests the size of the coherent scattering region is still increasing, even above 300 Å. These changes will clearly obscure any thickness-dependent measurements of the transport.

On the other hand, Figs. 1(b) and 1(d) show the RHEED data from Co/Ni superlattices. The full width at half maximum (FWHM), peak intensity, or diffuse background are independent of thickness between 50 and 1000 Å, showing that the film microstructure is maintained for all thicknesses. This is somewhat unexpected because film structure is usually expected to improve with increasing thickness. The cause of this uniform growth is unclear. We speculate that the usually found increase of coherent crystalline domains with increasing thickness may be deterred by: (a) the heteroepitaxy at interfaces, and (b) the domain size of Co buffer layers. The successful growth of Co/Ni superlattice films with uniform microstructure allows a study of the effect of surface phonon scattering on electrical resistivity.

According to Mathiessen's rule [14], the electrical resistivity can be expressed as a sum of the residual (ρ_0) and the temperature-dependent [$\rho_T(T)$] resistivities:

$$\rho = \rho_0 + \rho_T(T). \tag{1}$$

The low temperature behavior of $\rho_T(T)$ has been extensively studied for bulk elements [15]. The alkaline meals show T^5 dependence, a characteristic of electron-phonon scattering. However, this T^5 dependence has not been observed in the transition metals because of the enhanced electron-electron scattering due to the large density of states of d electrons at the Fermi level. The iron group elements (Fe, Co, Ni) show even more complicated behavior because of additional scattering processes of magnetic origin [16]. Nonetheless, the resistivities of bulk Co and Ni are apparently well described by the linear and quadratic terms in T. A few of our Co/Ni superlattice films, which we have measured the resistivity below 4.2 K, showed similar behavior. Therefore the low temperature data are difficult to analyze. However, the resistivity of many metals at intermediate temperatures (10–300 K), is surprisingly well described by a simple form, known as the Bloch-Grüneisen (B-G) model [16], which accounts for electron-phonon scattering in idealized monovalent metals with Debye phonon spectra and spherical Fermi surfaces.

$$\rho_T(T) = S(T/\theta_D)^5 J_5(\theta_D/T) \tag{2}$$

with

$$J_5(x) = \int_0^x [(e^z - 1)(1 - e^{-z})]^{-1} z^5\, dz\,, \tag{3}$$

where S is a material specific property and θ_D is the Debye temperature. Not all materials follow the simple Mathiessen's rule, and not all metallic superlattices have a temperature-dependent resistivity described by the B-G model. In addition, the resistivity of bulk Co and Ni is known to deviate from the B-G formula at high temperature close to the Curie temperature. However, the deviation is not yet significant at 300 K. In fact, the observed resistivity of Co/Ni superlattices is well described by this model between 10 to 300 K, indicating that electron-phonon scattering of the B-G model is the dominant mechanism in this temperature range.

The residual resistivity ρ_0 increases with decreasing d (d overall film thickness), as shown in the inset to Fig. 2, which is well described by the power law $\sim 1/d^{2.3}$ for $d < 500$ Å. This is consistent with a surface scattering mechanism of a quantum size effect [6]. It should be pointed out that this dependence is not a unique proof of surface scattering since, in many cases, the in-plane grain size may decrease with decreasing thickness. And thus it may mimic a similar thickness dependence.

Figure 2 shows the temperature-dependent resistivity ρ_T for a number of thicknesses. For $d > 300$ Å, no dependence was found on d or Λ, which suggests that electronic and phonon structure are affected little by either superlattice structure or total film thickness. However, for $d < 300$ Å, ρ_T increases rapidly as the films become thinner. Not only the magnitude but also the shape of ρ_T changes in the thinner films. The resistivity of the 85 Å thick film, for example, increases almost three times as fast as that of 300 Å or thicker films, while the resistivities of the films for $d > 300$ Å were virtually indistinguishable from the average resistivity of bulk Co and Ni [17]. Thinner films show a linear T dependence at lower temperature, which is characteristic of electron-phonon scattering for $T >$ Debye temperature and indicative of softening of the phonon modes.

ρ_T is well described by Eq. (2) in the temperature (10–300 K) and thickness ranges investigated, as shown in Fig. 3. There are only two adjustable parameters, θ_D the Debye temperature and S the scaling factor, material specific properties which may be calculated if the phonon dispersion relations are known. Note that the fit is excellent for all samples and temperature, although the magnitude of the resistivity and the temperature scale in reduced units vary by more than a factor of 2. This shows that the electron-phonon scattering as described by the B-G model is the dominant contributor to the temperature-dependent resistivity of our samples. The inset in Fig. 3 shows the same data in log-log plot. The deviation from the B-G model at low temperature is due to electron-electron scattering, exhibiting T^2 dependence. However, as the thickness decreases, the data tend to follow the B-G model more closely, suggesting the ever-increasing contribution from electron-phonon scattering. For $T > 0.2\theta_D$, excellent agreement was found in all samples between the data and the B-G model. Even

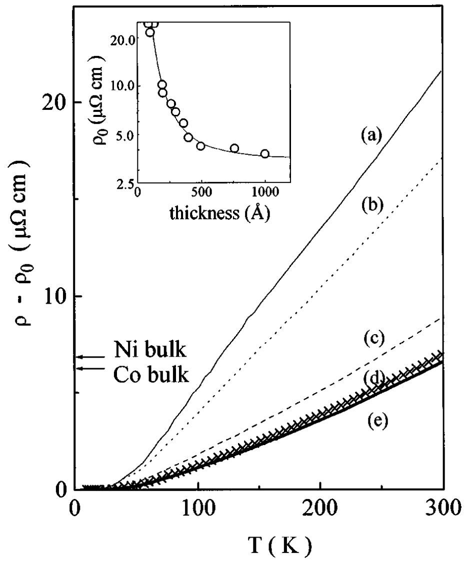

FIG. 2. Temperature-dependent resistivity ρ_T for various total film thicknesses. (a) 85, (b) 100, (c) 200 (d) 300, and (e) 1000 Å thick film. Inset: residual resistivity ρ_0. The solid line is a fit to a quantum size effect model.

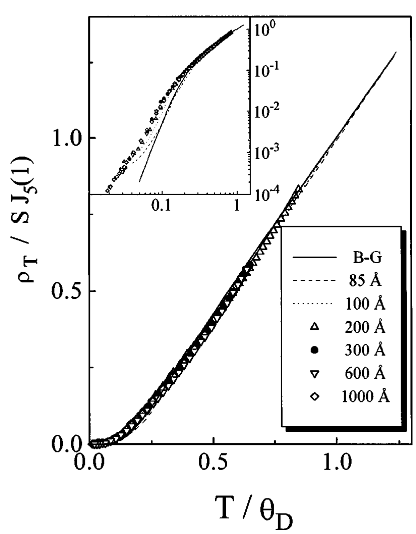

FIG. 3. Temperature-dependent resistivity ρ_T in reduced units. A solid line is a Bloch-Grüneisen model calculation. Inset: same data shown in log-log plot.

for $T < 0.2\theta_D$, the data show a clear trend toward the B-G model as the film thickness decreases.

Figures 4(a) and 4(b) show these parameters (θ_D and S) normalized to the values obtained from a 1000 Å thick film ($\theta_D \sim .450$ K), which are close to the known bulk parameters. The room temperature electrical resistivities of bulk Co and Ni are indicated by the arrows in Fig. 2. The Debye temperature of the thinnest film is reduced by almost half compared to the bulk Debye temperature, because surface phonons are softer than bulk phonons. This is consistent with other experiments, showing the surface phonon Debye temperature is about half that of the bulk [18]. The 40% increase in the scaling factor for the thinnest film suggests the presence of the two additional surface phonon modes, decaying fast into the bulk, which supports only three bulk acoustic phonon modes. It may also be a consequence of the relaxed selection rules for scattering processes due to the removal of momentum conservation normal to the surface. Therefore, the reduced Debye temperature and the increased scaling factor can be explained quantitatively as being due to surface phonon scattering.

In Fig. 4, the break in both parameters S and θ_D appears at $d \sim 300$ Å, close to the thickness where ρ_T starts to deviate from the bulk values (Fig. 2) and close to the estimated electronic mean free path (~260 Å) from an analysis of the residual resistivity ρ_0 [13]. We should stress that both ρ_T and ρ_0 show significant deviations from bulk values, for films thinner than the electronic mean free path, although they are governed by completely different processes.

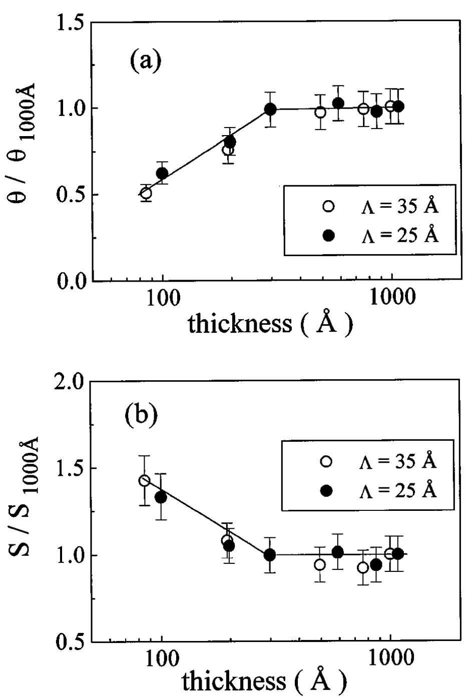

FIG. 4. (a) The Debye temperature and (b) the scale factor extracted from fits of the data to the Bloch-Grüneisen model for two different superlattice periods Λ. The values are normalized to the parameters found in 1000 Å thick film. The lines are guides to the eye.

In summary, Co/Ni superlattice films with a uniform microstructure independent of film thickness have been fabricated by molecular beam epitaxy. Because of this uniform film microstructure, the effect of surface phonon scattering in the electrical resistivity has been clearly observed. The sharp increase of the temperature-dependent resistivity for films thinner than the electronic mean free path can be attributed to a reduced effective Debye temperature and an increase in the number of phonon modes due to additional surface phonons. This is the first time that this effect has been clearly observed in the electrical resistivity of metallic films.

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