

## Increased "Bulk" NiO Resistivity in Fe<sub>3</sub>/NiO Modulated Structures as a Function of Modulation Wavelength

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Transverse electrical resistivities have been measured on Fe<sub>3</sub>O<sub>4</sub>/NiO modulated structures of varying modulation wavelength  $\Lambda$ . A dependence of the resistivity on  $\Lambda$  is observed in which the resistivity rapidly increases many orders of magnitude as the modulation wavelength decreases from the bulk  $\Lambda \rightarrow \infty$  limit in the vicinity of 600 Å. A qualitative argument is presented for a metal-insulator-metal interfacial-charge-transfer model which contains both the resistivity enhancement and the observed length scale dependence. [S0031-9007(96)00793-4]

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Low field dc electrical transport has been measured (perpendicular to the plane of the film) in Fe<sub>3</sub>O<sub>4</sub>/NiO modulated structures. There are many models for electrical transport through such a layered metal-to-insulator system. Transport may be limited by the bulk insulator properties, or by conditions at the Fe<sub>3</sub>O<sub>4</sub>/NiO interface. This latter case of emission limited transport results in the event that space charge regions are formed at the interface which inhibit the flow of mobile charge carriers in one or both directions (Schottky barriers, blocking contacts, *p-n* junctions, etc.). Such space charge regions result when mobile charge carriers are transferred from one material to the other to equilibrate the system Fermi level. The ability to deposit distinct Fe<sub>3</sub>O<sub>4</sub> and NiO layers on the scale of hundreds to tens of angstroms provides the opportunity to test these transport models over a wide range of length scales. What has been identified is an unanticipated, very abrupt, many order of magnitude increase in the Fe<sub>3</sub>O<sub>4</sub>/NiO modulated structure resistivities in the vicinity of a 300 Å layer thickness. The observed length scale dependence of the sample resistivities is not predicted by the appropriate bulk or interfacial transport models. In this Letter this anomalous effect is presented, and then a qualitative model is developed as a possible explanation of both the enhanced bulk NiO resistivity and observed length scale dependence.

Plasma assisted molecular beam epitaxy was employed for sample fabrication. Details of sample growth and structural characterization of these films are published elsewhere [1,2]. Previous studies on these modulated structure films have included magnetic susceptibility [3], dielectric response [4], and the in-plane versus out-of-plane anisotropy in electrical conduction [5]. The modulated structures fabricated for this research have Fe<sub>3</sub>O<sub>4</sub> and NiO layers of equal thickness. The targeted layer thicknesses for these samples range from 8 to 1768 Å. The number of bilayer repeats was chosen in order to maintain a constant total sample thickness targeted at 3346 Å. All bilayers consist of a Fe<sub>3</sub>O<sub>4</sub> layer followed by a NiO layer so that each film starts with

Fe<sub>3</sub>O<sub>4</sub> and ends with NiO. The oxides were deposited on polished single crystal MgO(001) substrate (with the dimensions 5 × 10 × 0.5 mm), which had been coated with 1000 Å of epitaxially deposited Ni(001).

This research involved two periods of sample fabrication. The films fabricated during the first growth series (series A films) included the following targeted modulation wavelengths (and bilayer repeats): 17 Å (200), 34 Å (100), 67 Å (50), 134 Å (20), 334 Å (10), 670 Å (5), 1673 Å (2). The second growth series (series B films) duplicated the four largest modulation wavelength samples of series A, and included a new film with  $\Lambda = 3346$  Å (1). The series B samples were grown on better quality substrates than the substrates used for the series A samples. This resulted in the series B films possessing superior long range structural coherence as manifested in the x-ray data [2].

Sample resistance was measured with pulsed dc current transverse to the plane of the films. The resistivities reported here are taken from an observed field independent low voltage range of 0.02 to 0.05 V (or a field of 300 to 750 V/cm). Transverse sample resistivities were measured for series A samples from 310 to 150 K. Series B films were significantly more resistive than series A samples, providing further evidence of their superior structural order. Unfortunately, these films were too resistive to take transport data below room temperature.

Fe<sub>3</sub>O<sub>4</sub> has a dc resistivity on the order of 10<sup>-2</sup> Ω cm at room temperature, and this magnitude could be used to categorize Fe<sub>3</sub>O<sub>4</sub> as either a poor metal or a highly doped (or dirty) semiconductor [6,7]. Stoichiometric NiO has a resistivity on the order of 10<sup>13</sup> Ω cm at 300 K [8]. Reported resistivities for NiO cover many orders of magnitude below this [6,9,10] as this extrinsic conduction is highly sensitive to individual sample impurity and/or defect concentration. The transport mechanism in NiO is thought to be variable range hopping conduction, but this is a much debated subject [9,11].

There are a number of possible transport mechanisms which may describe transverse electrical transport in

the  $\text{Fe}_3\text{O}_4/\text{NiO}$  modulated structures under study. If an Ohmic contact is formed at the  $\text{Fe}_3\text{O}_4/\text{NiO}$  interface, the transverse resistivity is expected simply to be an average of  $\rho_{\text{Fe}_3\text{O}_4}$  and  $\rho_{\text{NiO}}$  ( $\approx \rho_{\text{NiO}}/2$ ). Such bulk limited transport is expected to show no dependence on the modulation wavelength  $\Lambda$ .

Tunneling through the NiO layers may occur for the smallest modulation wavelength samples [12] and would be evidenced by a sharp reduction in  $\rho$  with decreasing  $\Lambda$ . In the literature, such metal-insulator-metal systems are most often studied in terms of tunneling processes [13–15]. High field transport mechanisms such as field assisted thermal ionization (Poole-Frenkel effect) [16], or electrode to bulk limited processes [12], are not relevant to these low voltage (field independent) resistivity measurements.

In the absence of tunneling, if a blocking contact exists at the  $\text{Fe}_3\text{O}_4/\text{NiO}$  interface the resulting current density at low voltages is given by the purely thermal process of Schottky emission over the interfacial barrier  $\phi_i$  [eV] [17–19]. The “zero field” areal resistivity (per interface)  $RA$  (where  $R$  [ $\Omega$ ] is transverse resistance and  $A$  is the interfacial contact area [ $\text{cm}^2$ ]) due to a blocking contact at a metal-to-insulator interface is given by [20]

$$RA = \frac{ke\phi_i/kT}{120T} = 7.2 \times 10^{-7} T^{-1} e^{\phi_i/kT} [\Omega \text{ cm}^2], \quad (1)$$

where  $T$  is the temperature in kelvin and  $k$  is the Boltzmann factor [eV/K]. In this case the sample resistivities are a function of the interfacial barrier  $\phi_i$  and may significantly exceed that of  $\rho_{\text{NiO}}$ . Because the number of interfaces for these samples is given by  $2 \times 3346/\Lambda$ , in this scenario the sample resistivities are expected to increase linearly with decreasing  $\Lambda$ .

Resistivity measurements were also made on several pure  $\text{Fe}_3\text{O}_4$  and NiO films during both growth series. The room temperature transverse resistivities of these pure films were well reproduced at the values of  $10^{-2} \Omega \text{ cm}$  for  $\rho_{\text{Fe}_3\text{O}_4}$ , and  $10^6 \Omega \text{ cm}$  for  $\rho_{\text{NiO}}$ . The transverse modulated structure resistivities for both sample series A and B are shown in Fig. 1. Note that there is a limiting value for the modulated structure resistivities in the  $\Lambda \rightarrow \infty$  limit of  $\rho_{\text{NiO}}/2$ . For this reason, dotted lines are shown which approach this limiting value, and it is important to realize that this is the magnitude of the resistivity expected for all samples ( $\Lambda$  values) in the absence of interfacial resistance and/or nonlocality effects. Both sample sets demonstrate a dramatic wavelength dependent increase in resistivity above that of bulk NiO. The transverse resistivity peaks for series A samples at  $334 \text{ \AA}$  with almost 4 orders of magnitude increase, and for series B samples at  $670 \text{ \AA}$  an increase above the  $\Lambda \rightarrow \infty$  limit of nearly a factor of  $10^6$  is observed.

The increase in  $\rho$  with decreasing  $\Lambda$  observed in Fig. 1 may suggest that the NiO layers possess a local resistivity function which increases near the  $\text{Fe}_3\text{O}_4/\text{NiO}$

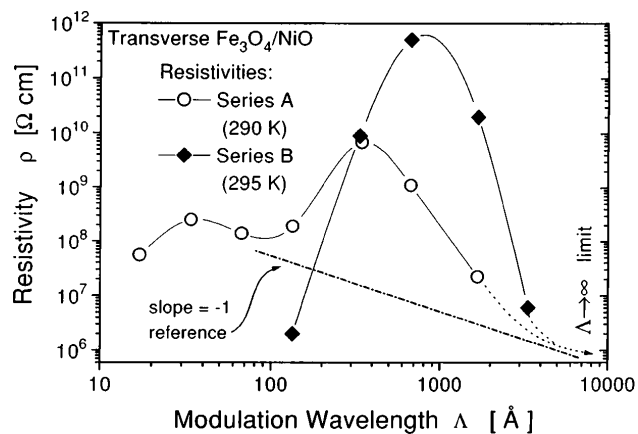


FIG. 1. Transverse  $\text{Fe}_3\text{O}_4/\text{NiO}$  modulated structure resistivities (series A and B samples) at room temperature. The dotted lines indicate that, in the  $\Lambda \rightarrow \infty$  limit,  $\rho$  approaches the value of  $\rho_{\text{NiO}}/2$ .

interface. In this case, samples with the thinner layers would possess larger average (measured) resistivities, and this would result (qualitatively) in the type of length scale dependence which is observed. However, a single local resistivity function cannot be used to quantitatively describe the NiO resistivity in each of these samples. If this were the case, the slope of the increase in average resistivity as  $\Lambda$  decreases would be limited to a negative one in this log-log figure (see dashed line in Fig. 1), regardless of how abrupt the change in (or how negative the slope of) the local resistivity function [2]. For this reason, it is incorrect to consider a single resistivity function which varies locally as a possible explanation for the observed length scale dependence.

The measured resistivities clearly exceed that of the pure NiO films, and this suggests the presence of some form of interfacial resistance. The series A sample resistivity data taken as a function of temperature were fitted by Eq. (1) to determine if these data are consistent with Schottky emission over blocking contacts at the  $\text{Fe}_3\text{O}_4/\text{NiO}$  interfaces. While Eq. (1) provides the areal resistivity per interface, because these samples possess a number of interfaces given by  $3346 \text{ \AA}/\Lambda$ , the quantity  $\rho \Lambda$  [ $\Omega \text{ cm}^2$ ] represents the areal resistivity per interface for a given sample. The top half of Fig. 2 shows the best fits of Eq. (1) to the temperature dependent data for two series A samples. Such fitting yields the best fit parameter values for the prefactors  $P$  [ $\Omega \text{ cm}^2 \text{ K}$ ] and activation energies  $\phi_i$  [eV]. These fitting parameters are shown for all series A samples in the bottom graph of Fig. 2. The sharp disagreement between the prefactors resulting from these fits and the theoretical value of  $7.2 \times 10^{-7} \Omega \text{ cm}^2$  is a clear indication that the standard model of thermionic emission over a barrier at the  $\text{Fe}_3\text{O}_4/\text{NiO}$  interface cannot be used to explain these data.

Looking at the bottom graph of Fig. 2, we see that the activation energies of the modulated structure films have

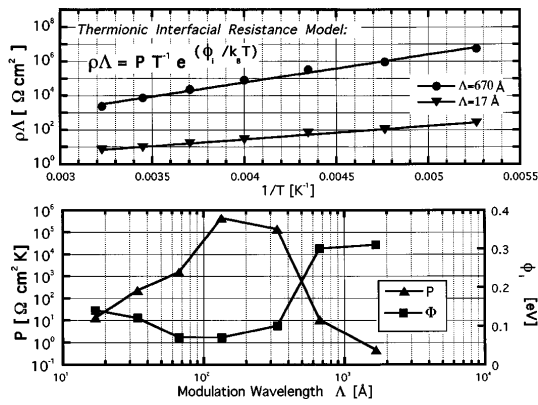


FIG. 2. (Top) Temperature dependent data and best fit line of Eq. (1) for two samples from growth series A. (Bottom) The parameters extracted from such fitting for all series A samples.

roughly the two values of 0.1 and 0.3 eV. The resistivity of series A pure NiO films were also measured as a function of temperature. A thermal activation energy of 0.3 eV was measured from these films, and this value is in agreement with the literature [21]. It is interesting to note that the transport in the larger modulation wavelength samples demonstrates a temperature dependence comparable to NiO, indicating bulk (NiO) limited transport. However, as  $\Lambda$  decreases, beginning at 334 Å, there is an abrupt decrease in  $\phi_i$  to approximately 0.1 eV. This reduction in temperature dependence coincides with a sharp reduction in sample resistivities beginning below 334 Å. This may be evidence of the onset of a new conduction mechanism (possibly tunneling) in competition with whatever mechanism is causing  $\rho$  to increase as  $\Lambda$  decreases from the bulk limit. While the observed activation energies should not be thought of as actual interfacial potentials, these values can be taken as the upper limit for any interfacial barriers which may exist, and tunneling over this barrier height at this length scale is plausible [12].

The increase in  $\rho$  above  $\rho_{\text{NiO}}$  as  $\Lambda$  decreases from the  $\Lambda \rightarrow \infty$  limit is an unexpected and puzzling feature. It has been noted that this feature, demonstrated independently by both sample sets, is too abrupt to be explained by assuming that a single function for the local NiO resistivity is applicable to each sample. Rather, these data suggest that each sample is characterized by an independent resistivity function which is increased dramatically as  $\Lambda$  decreases in the vicinity of 300 to 600 Å from the  $\Lambda \rightarrow \infty$  limit. In the remainder of this Letter we present a simple model in which the insulator's mobile charge carriers move across the interface into the metal in order to equilibrate the system Fermi energy. In this model, however, transport is not limited by the barrier at the interface. Rather, the formation of this blocking contact results in a length scale dependent enhancement of the insulator's bulk resistivity such as observed in Fig. 1.

Simmons pointed out (in 1965) that, even if a blocking contact exists in a metal-to-insulator junction, electrical

transport may remain limited by the bulk insulator resistivity  $\rho_B$  [22]. In this case, charge carriers are not passed through the interfacial barrier and insulator without energy loss because the mean free path of the mobile charge carriers is comparable to, or less than, the insulator thickness. In terms of the barrier energy  $\phi_i$ , the condition that a blocking contact exists, but transport remains bulk limited, may be written [from Eq. (1)] as

$$0 < \phi_i < kT[\ln \rho_B + \ln \ell + \ln T + 14] \text{ [eV]}, \quad (2)$$

where  $\ell$  is the insulator thickness in cm. At room temperature (300 K), and using  $\rho_{\text{NiO}} = 10^6$  Ω cm, we may conclude from Eq. (2) that if a blocking contact exists at the Fe<sub>3</sub>O<sub>4</sub>/NiO interface with a barrier energy  $\phi_i$  less than 0.86 eV, then transport will remain bulk limited (for all modulation wavelength samples).

If a blocking contact is formed, by definition, the insulator loses a fraction of its mobile charge carriers to the space charge regions at the interface. Assuming a constant mobility, and using  $10^6$  Ω cm as the value of  $\rho_{\text{NiO}}$ , one may extrapolate from the work of Bosman and Crevecoeur [23] (which was a study of NiO resistivity as a function of Li doping) to estimate  $N$ , the number of free charge carriers per unit volume in the NiO under study. This result (which should be considered only an order of magnitude estimate) is  $N \approx 2 \times 10^{17}$  cm<sup>-3</sup>. This value for  $N$  may be used, in conjunction with a NiO relative dielectric constant of  $K = 8$  [6], to estimate the length of the depletion region  $\lambda$  resulting from a given interfacial barrier energy  $\phi_i$ . This calculation [12] for the relatively small interfacial barrier range of  $\phi_i = 0.1$  to 0.25 eV, for example, yields depletion lengths  $\lambda$  of approximately 200 to 300 Å. Because each NiO layer is sandwiched between two Fe<sub>3</sub>O<sub>4</sub> layers, this corresponds to 400 to 600 Å of total depleted region in a single layer. The purpose of this discussion is to show that, if a blocking contact is formed at the Fe<sub>3</sub>O<sub>4</sub>/NiO interface, the depletion length may permeate the entire NiO layers (so that  $\Lambda < 4\lambda$ ) in many of the Fe<sub>3</sub>O<sub>4</sub>/NiO modulated structure under study.

In the above discussion, the assumption was made that the depletion region experienced 100% loss of its mobile charge carriers. In reality, some fraction  $\alpha$  will be lost to the interfacial-charge-transfer process. Thus, in the event  $\Lambda < 4\lambda$ , the resistivity enhancement of the NiO layers resulting from the formation of the blocking contact may be written as

$$\rho = \frac{1}{(N - \alpha N)\mu q_e} = \frac{\rho_B}{1 - \alpha} \text{ [Ω cm]}, \quad (3)$$

where  $\mu$  is the carrier mobility and  $q_e$  its charge, and  $\rho_B$  is the bulk insulator resistivity [Ω cm].

We now show how this simple concept yields the observed length scale dependence. Consider a blocking contact at a metal-to-insulator junction in the bulk  $\Lambda \rightarrow \infty$  limit. The depletion region extends some distance  $\lambda_B$  into the insulator, and in this region there is an average

fractional loss  $\alpha_B$  of the number of mobile charge carriers per unit volume  $N$  of the insulator. The fractional loss of  $\alpha_B$  charge carriers over the length  $\lambda_B$  creates interfacial-space-charge regions with an electrostatic potential which precisely offsets the difference in the metal and insulator chemical potentials.

Now consider the case in which  $\Lambda$  is decreased, so that  $\Lambda < 4\lambda_B$ . In this case, the space charge regions are constrained to a smaller length scale, and the resulting interfacial potential will be reduced. If we assume there is no change in the difference in chemical potentials as  $\Lambda$  decreases, then the same electrostatic potential must now be effected over a smaller distance. This leads to the requirement that more charge per unit volume be transferred from the insulator to the interfacial-space-charge regions in order to affect the same potential  $\phi_i$  over the reduced distance. It should be mentioned that, strictly speaking, the assumption that the interfacial barrier  $\phi_i$  is constant as  $\Lambda$  decreases must be in error because the  $\Lambda \rightarrow 0$  limit requires that  $\phi_i \rightarrow 0$ . Therefore this simple model is incomplete.

The relationship between the fractional loss of mobile charge carriers  $\alpha$  and the modulation wavelength  $\Lambda$  may be found by approximating the space charge regions at the interface by using a parallel plate capacitor model [20]. This result is

$$\alpha = (4\lambda_B/\Lambda)^2 \alpha_B, \quad (4)$$

and Eq. (3) becomes

$$\rho = \frac{\rho_B}{[1 - (4\lambda_B/\Lambda)^2 \alpha_B]} [\Omega \text{ cm}]. \quad (5)$$

Equation (5) must remain positive finite, and this may be understood in terms of the resistivity reaching the stoichiometric limit as virtually all impurity and/or defect carriers are lost to interfacial charge transfer at the limiting modulation wavelength  $\sqrt{\alpha_B} 4\lambda_B$ .

This model is in excellent agreement with the data that it predicts an extremely rapid increase in resistivity to the stoichiometric limit as virtually all the free charge carriers are lost in a very narrow range of decreasing modulation wavelength. Insight, concerning how rapid the increase in  $\rho$  (with decreasing  $\Lambda$ ) predicted by this model, can be gained by assuming, for example, a value of  $\alpha_B = 90\%$  and using the estimated value for  $N$  above. In this case, the  $\text{Fe}_3\text{O}_4/\text{NiO}$  modulated structure resistivity is expected to climb from the bulk NiO value of  $10^6 \Omega \text{ cm}$  to the stoichiometric value of  $10^{13} \Omega \text{ cm}$  as the modulation wavelength decreases in the narrow range of 800 to 650 Å. From this result, it is clear this simple model can provide qualitative agreement with the  $\text{Fe}_3\text{O}_4/\text{NiO}$  modulated structure resistivities of Fig. 1.

This process is not expected to be unique to the  $\text{Fe}_3\text{O}_4/\text{NiO}$  system. Any metal-to-insulator junction which forms a blocking contact with an interfacial barrier that satisfies Eq. (2) has the potential to manifest such increased and length scale dependent resistivities. This effect suggests the possibility of achieving significant improvement in the resistive properties of insulating layers by reducing their thickness and coating (or layering) them with some other material which extracts its mobile charge carriers.

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