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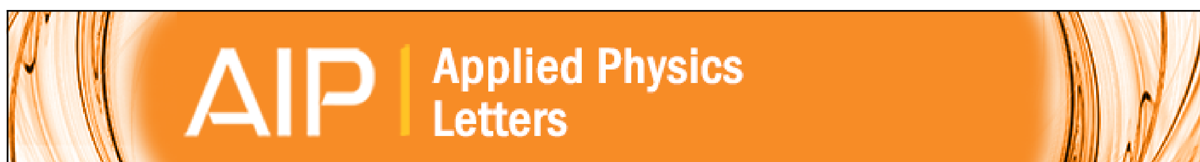

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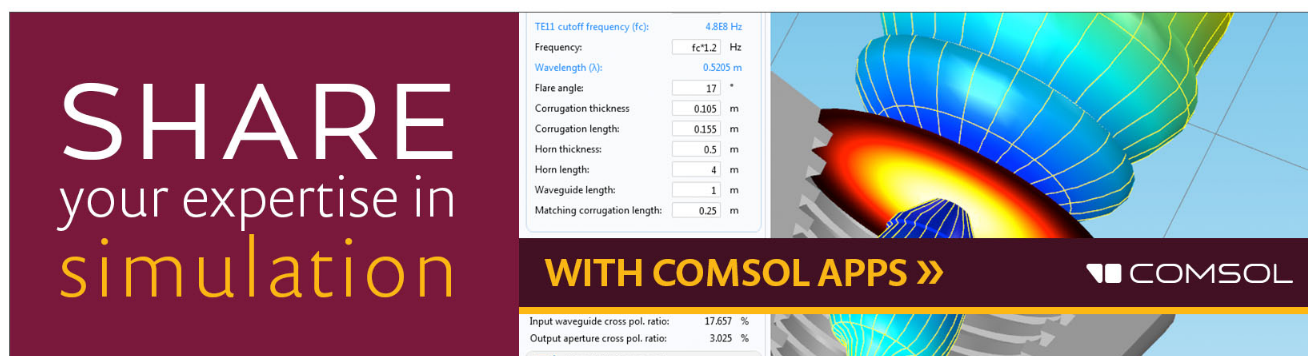

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APPLIED PHYSICS LETTERS **92**, 012118 (2008)

Measurement of electronic structure at nanoscale solid-solid interfaces by surface-sensitive electron spectroscopy

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We explore the use of electron spectroscopy that samples the near-surface region of a crystal to study the electronic structure at the buried interfaces between two dissimilar transition-metal oxides. The interface is probed by comparing experimental ultraviolet photoelectron spectra to model spectra and by taking sequential differences between the experimental spectra as one oxide is grown on another. Using (100) Fe_3O_4–NiO and Fe_3O_4–CoO interfaces grown by molecular beam epitaxy, we show that there is a much higher density of electronic states at the Fe_3O_4–CoO interface than at the Fe_3O_4–NiO interface. The origin of this difference is discussed. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2831000]

The properties of the interfaces between two materials can have a significant effect on a wide range of device characteristics, especially for nanoscale devices. Some of the properties of buried interfaces can be determined by using transmission electron microscopy to probe a cross section of the sample. Other scattering techniques such as x-ray or neutron diffraction and reflection[1,2] have also been used. However, those techniques do not give direct information on the interfacial electronic structure. Recently, Holmstrom *et al.*[3] proposed a characterization technique based on atomic core-level shifts to analyze the interfacial quality of layered structures; high kinetic-energy photoelectron spectroscopy is used so that the electrons have long mean-free paths and sample information from embedded interface layers. In pioneering work, Gonzalez-Elipe and Yubero[4] used several spectroscopic techniques to study oxide-oxide interfaces. They focused on the investigation of chemical states and bonding configurations at the interfaces, mostly by probing the Auger parameter measured by x-ray photoemission.[4]

Low kinetic-energy photoelectron spectroscopies that are very surface sensitive have rarely been used to probe the electronic structure at a buried interface, due to the short photoelectron inelastic mean-free path. In this letter, we demonstrate that the detailed information about interface electronic properties can be obtained by using ultraviolet photoelectron spectroscopy (UPS) combined with layer-by-layer growth of one material onto another. UPS was chosen because, although for photon energies of 20–50 eV, the photoexcited electrons originate from only the outermost few monolayers of the surface, it gives the most complete information about the valence band electronic structure near Fermi level, the energy region that is important in all device applications.

Since UPS spectra sample several monolayers below the surface of a sample, spectra measured for ultrathin films deposited onto a substrate will consist of a superposition of emission from the substrate, any interfacial states that may be present, and the overlayer film, with each weighted by the electron mean-free path, λ,

$$I(d) = I_0^{\text{substrate}} \exp[-(d+d_{\text{is}})/\lambda] + I_0^{\text{overlayer}} \times\{1-\exp[-(d-d_{\text{io}})/\lambda]\} + I_0^{\text{interface}} \times\{1-\exp[-(d_{\text{is}}+d_{\text{io}})/\lambda]\}\exp[-(d-d_{\text{io}})/\lambda], \quad (1)$$

where $I_0^{\text{substrate}}$ and $I_0^{\text{overlayer}}$ are the UPS spectra for semi-infinite samples of each material, $I_0^{\text{interface}}$ is the spectral intensity for the interface layer, scaled to a semi-infinite slab having the interfacial electronic structure, d_{is} and d_{io} are the thickness of the substrate and overlayer, respectively, that are involved in forming the interface layer, and d is the total thickness of the overlayer deposited. (λ is the only adjustable parameter in Eq. (1); it is chosen to best fit the experimental data. The values obtained range from about 0.6 to 0.8 nm, close to what would be expected from the "universal curve" of electron mean-free paths in solids.[5] The variation is due to inaccuracies in determining the overlayer film thickness and has no significant effect on the results obtained for interfacial electronic structure.) If no interface states are present, i.e., $d_{\text{is}}=d_{\text{io}}=0$, Eq. (1) can be simplified to

$$I_0(d) = I_0^{\text{substrate}} \exp(-d/\lambda) + I_0^{\text{overlayer}}[1-\exp(-d/\lambda)]. \quad (2)$$

Difference spectra $\Delta I\ (d)$, obtained by subtracting Eq. (2) from the measured UPS spectra $I(d)$,

$$\Delta I(d) = I(d) - I_0(d), \quad (3)$$

thus, give some information about the interface states. If the values of d_{is} and d_{io} were known, the interface spectrum $I_0^{\text{interface}}$ could then be determined from

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$$I_0^{\text{interface}} = \frac{\Delta I(d) + I_0 - I_0^{\text{substrate}} \exp[-(d+d_{\text{is}})/\lambda] - I_0^{\text{overlayer}}\{1-\exp[-(d-d_{\text{io}})/\lambda]\}}{\{1-\exp[-(d_{\text{is}}+d_{\text{io}})/\lambda]\}\exp[-(d-d_{\text{io}})/\lambda]}. \quad (4)$$

In our work, electronic properties at the Fe_3O_4–NiO and Fe_3O_4–CoO interfaces have been investigated. Fe_3O_4 is a metallic ferrimagnet, and both NiO and CoO are insulating antiferromagnets. The exchange biasing effect,[6,7] in which the hysteresis loop of a ferro- or ferrimagnet is shifted asymmetrically along the field axis when in contact with an antiferromagnetic material, has been observed for both interfaces, making them interesting for spintronics. NiO and CoO have the same rocksalt crystal structure, and, although Fe_3O_4 has the inverse spinel structure, both structures share a common face-centered-cubic oxygen sublattice, where the lattice mismatch is only 0.55% between Fe_3O_4 and NiO and 1.45% between Fe_3O_4 and CoO. Although NiO and CoO have very similar bulk electronic properties, we will demonstrate that the interface electronic structure is significantly different between these two systems.

Experimental UPS spectra (He II; $h\nu = 40.84$ eV) are measured as from 1 to 20 ML of NiO (100) [Fig. 1(a)] or CoO (100) [Fig. 2(a)] and are grown heteroepitaxially onto Fe_3O_4 (100) substrates, using oxygen-plasma-assisted molecular-beam epitaxy.[8,9] [1 ML of NiO (100)=0.208 nm; 1 ML of CoO (100)=0.213 nm.] An inelastic Li background[10] has been subtracted from the experimental spectra. Figures 1(b) and 2(b) show the model spectra computed using Eq. (2), where the experimental UPS spectra of Fe_3O_4 and the 20 ML NiO or CoO film are used for $I_0^{\text{substrate}}$ and $I_0^{\text{overlayer}}$, respectively.[8] The difference spectra in Fig. 1(c) are obtained by subtracting each spectrum in Fig. 1(b) from the corresponding one in Fig. 1(a); the same is done in Fig. 2(c). The differences between measured and model spectra are much larger in Fig. 2(c) than in Fig. 1(c). This indicates that a higher density of electronic states is present at the Fe_3O_4–CoO interface than at the Fe_3O_4–NiO interface.

The development of interfacial electronic structure can be seen by taking sequential differences between the experimental UPS spectra as each additional overlayer is deposited onto the Fe_3O_4. The electronic structure of the jth layer $I_{j\text{th}}$ can then be determined by subtracting the total intensity I_i (after the ith layer is grown), corrected for attenuation by the thickness of the jth layer d_j from the total intensity I_j (after the jth layer is deposited),

$$I_{j\text{th}} = I_j - I_i \exp(-d_j/\lambda). \quad (5)$$

The resultant first, second, and third layer structures are shown in Fig. 1(d) for the NiO films and in Fig. 2(d) for the CoO films. The areas of their spectra have been normalized to that of the 20 ML bulk-like overlayer spectrum. The spectral shapes of the thin NiO films are very similar to that of the thickest, bulk-like NiO layer, even for the first monolayer film. For CoO, the spectra are nearly identical to bulklike from the second monolayer of CoO; however, the features in the first monolayer film are very different, especially those around a binding energy of 10 eV. This further confirms that the density of interfacial electronic states is much higher for Fe_3O_4–CoO than for Fe_3O_4–NiO.

The density of interface states is very small for Fe_3O_4–NiO.[8] Even for Fe_3O_4–CoO, the interface involves only the first monolayer of CoO and does not extend appreciably into the rest of the CoO layer [Fig. 2(d)]. We, thus,

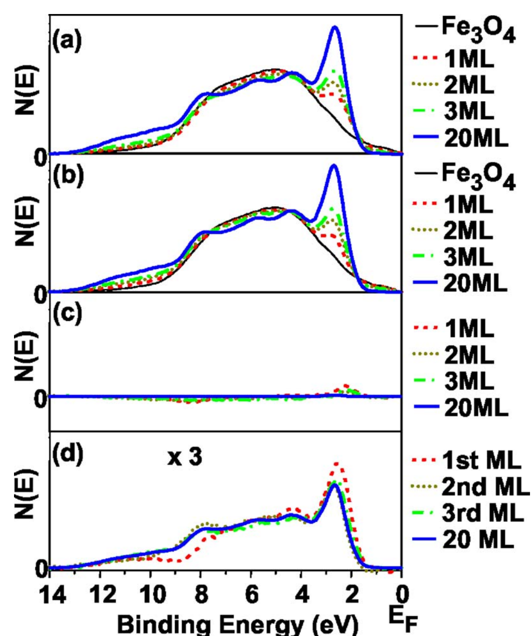

FIG. 1. (Color online) (a) Experimental and (b) model UPS spectra of NiO films grown on Fe_3O_4. An inelastic Li background (see Ref. 10) has been subtracted from the experimental spectra. (c) Difference spectra taken by subtracting model spectra from measured spectra. (d) Sequential differences taken from (a).

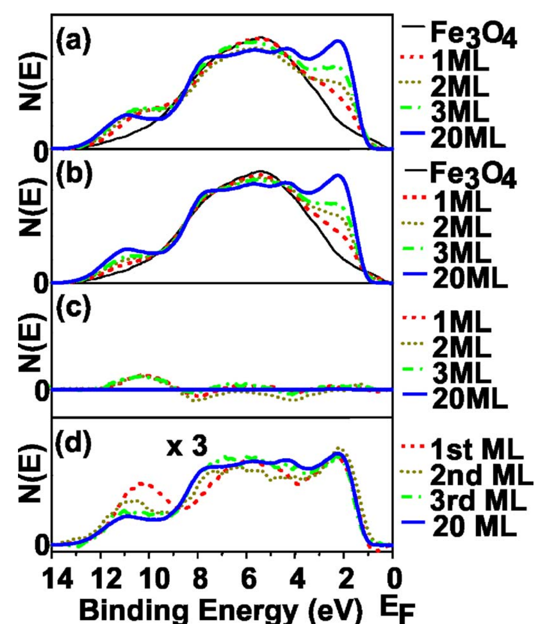

FIG. 2. (Color online) (a) Experimental and (b) model UPS spectra of CoO films grown on Fe_3O_4. An inelastic Li background (see Ref. 10) has been subtracted from the experimental spectra. (c) Difference spectra taken by subtracting model spectra from measured spectra. (d) Sequential differences taken from (a).

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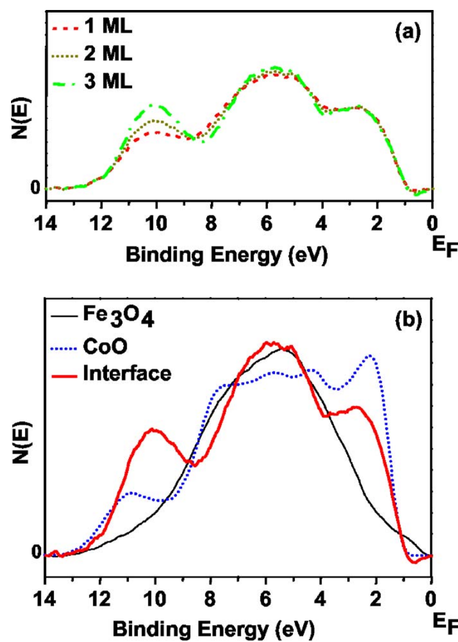

FIG. 3. (Color online) (a) The calculated $I_0^{\text{interface}}$ spectra using Eq. (4). (b) Comparison of the spectra for the Fe_3O_4 substrate, the thickest CoO film [both from Fig. 2(a)] and the interface electron state, averaged from the three spectra in (a).

assume that the interface region for Fe_3O_4–CoO involves only the first monolayer of CoO and the top monolayer of the Fe_3O_4, i.e., $d_{is}=d_{io}=1$ ML. Using the difference spectra for 1, 2, and 3 ML in Fig. 2(c) as ΔI (d) in Eq. (4), three respective interface state spectra $I_0^{\text{interface}}$ are obtained [Fig. 3(a)]. The similarity of the three spectra indicates that our interface model is close to the actual case. Averaging the three spectra in Fig. 3(a) yields the thick solid spectrum in Fig. 3(b), which is our best determination of the electronic structure at the Fe_3O_4–CoO interface. It is very different from those of either the Fe_3O_4 substrate (thin solid line) or the CoO overlayer (dotted line).

Our approach represents a promising new probe for identifying embedded interface electronic states. One of the reasons why the Fe_3O_4–NiO interface is electronically sharper than the Fe_3O_4–CoO interface could be strain due to the larger lattice mismatch, although that strain is still very small. Another reason could be the difference in d orbital configuration of Ni^{2+} ($3d^8$) and Co^{2+} ($3d^7$). The t_{2g} band is filled for Ni^{2+},[11] but it is missing one electron for Co^{2+}.[12] For the Fe ions in octahedral sites, the t_{2g} band is half filled for Fe^{3+} ($3d^5$) but has one additional electron for Fe^{2+} ($3d^6$). When very thin CoO films are deposited onto the Fe_3O_4 substrate, charge transfer may occur by removing one electron from the t_{2g} band of Fe^{2+} to fill that of Co^{2+}. The resulting $3d^5$ configuration of Fe^{3+} is generally the lowest energy state for iron compounds. $Fe^{2+} \rightarrow Co^{2+}$ electron transfer may thus be the origin of the interface states that we have observed.

In summary, by analyzing the evolution of UPS spectra as from one to several monolayer of NiO or CoO are grown heteroepitaxially on Fe_3O_4 we have shown that interface electronic states can be identified by comparing the experimental spectra to model spectra. This method, when used appropriately, can be applied to determine the interface structure of a variety of substrate-overlayer systems, including metals and semiconductors. Such a method can also be applied using any technique whose probe information is attenuated by overlayer thickness (e.g., x-ray photoemission spectroscopy or Auger).

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[1] H. Zabel, Appl. Phys. A: Solids Surf. **58**, 159 (1994).
[2] Z. H. Mai, G. M. Luo, C. X. Liu, M. H. Li, H. W. Jiang, W. Y. Lai, J. Wang, Y. F. Ding, T. P. A. Hase, B. D. Fulthorpe, and B. K. Tanner, Nucl. Instrum. Methods Phys. Res. B **199**, 494 (2003).
[3] E. Holmstrom, W. Olovsson, I. A. Abrikosov, A. M. N. Niklasson, B. Johansson, M. Gorgoi, O. Karis, S. Svensson, F. Schäfers, W. Braun, G. Öhrwall, G. Andersson, M. Marcellini, and W. Eberhardt, Phys. Rev. Lett. **97**, 266106 (2006).
[4] A. R. Gonzalez-Elipe and F. Yubero, in *Handbook of Surfaces and Interfaces of Materials*, edited by H. S. Nalwa (Academic, New York, 2001), vol. 2, p. 141, and references therein.
[5] M. P. Seah and W. A. Dench, Surf. Interface Anal. **1**, 2 (1979).
[6] P. A. A. van der Heijden, C. H. W. Swüste, W. J. M. de Jonge, J. M. Gaines, J. T. W. M. van Eemeren, and K. M. Schep, Phys. Rev. Lett. **82**, 1020 (1999); J. A. Borchers, Y. Ijiri, D. M. Lind, P. G. Ivanov, R. W. Erwin, S. H. Lee, and C. F. Majkrzak, J. Appl. Phys. **85**, 5883 (1999); J. A. Borchers, Y. Ijiri, D. M. Lind, P. G. Ivanov, R. W. Erwin, A. Qasba, S. H. Lee, K. V. O'Donovan, and D. C. Dender, Appl. Phys. Lett. **77**, 4187 (2000).
[7] T. Terashima and Y. Bando, Thin Solid Films **152**, 455 (1987); R. M. Wolf, A. E. M. De Veirman, P. van der Sluis, P. J. van der Zaag, and J. B. F. aan de Stegge, *Epitaxial Oxide Thin Films and Heterostructures*, MRS Symposia Proceedings No. 347, edited by D. K. Fork, J. M. Phillips, R. Ramesh, and R. M. Wolf (Materials Research Society, Pittsburgh, 1994), p. 23.
[8] H. Q. Wang, W. Gao, E. I. Altman, and V. E. Henrich, J. Vac. Sci. Technol. A **22**, 1675 (2004).
[9] H. Q. Wang, E. I. Altman, and V. E. Henrich (unpublished).
[10] X. Li, Z. Zhang, and V. E. Henrich, J. Electron Spectrosc. Relat. Phenom. **63**, 253 (1993).
[11] H. Takahashi, F. Munakata, and M. Yamanaka, J. Phys.: Condens. Matter **7**, 1583 (1995).
[12] M. HaBel, H. Kuhlenbeck, H.-J. Freund, S. Shi, A. Freitag, V. Staemmler, S. Liitkehoff, and M. Neumann, Chem. Phys. Lett. **240**, 205 (1995).

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