

Sample Preserving Deep Interface Characterization Technique

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We propose a nondestructive technique based on atomic core-level shifts to characterize the interface quality of thin film nanomaterials. Our method uses the inherent sensitivity of the atomic core-level binding energies to their local surroundings in order to probe the layer-resolved binary alloy composition profiles at deeply embedded interfaces. From an analysis based upon high energy x-ray photoemission spectroscopy and density functional theory of a Ni/Cu fcc (100) model system, we demonstrate that this technique is a sensitive tool to characterize the sharpness of a buried interface. We performed controlled interface tuning by gradually approaching the diffusion temperature of the multilayer, which lead to intermixing. We show that core-level spectroscopy directly reflects the changes in the electronic structure of the buried interfaces, which ultimately determines the functionality of the nanosized material.

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Thin film nanodevices such as multilayers and superlattices represent numerous new opportunities in materials science. Their unique properties arise from the introduction of interfaces and the emergence of finite size effects due to quantum interference [1–6]. The interfaces represent tunable parameters, where interface composition or film thickness and geometry can be used to alter various magnetic, optical, and mechanical properties.

A range of methods to describe multilayer interface properties exist which can coarsely be divided into destructive and nondestructive techniques. In destructive methods such as mass spectrometry and microscopy techniques (e.g., transmission electron microscopy [7] and its variants), it is necessary to destructively modify the samples in some way in order to obtain the desired information. Nondestructive methods include scattering techniques such as x-ray or neutron diffraction and reflection [8,9]. However, interface information at the atomic scale is difficult to obtain. Moreover, while other techniques such as scanning tunneling microscopy and atomic force microscopy provide local structural information, these methods are generally limited to surface analysis and cannot reliably describe buried interface qualities [10,11]. Surface sensitivity is also strongly associated with photoelectron spectroscopy due to the short mean free path of electrons with kinetic energies in the range of 50–500 eV [12].

In this Letter we propose a new nondestructive characterization technique to analyze the interfacial quality of layered structures based on previous theoretical predictions [1,13]. The method relies upon accurate measurements of chemical shifts in core levels [14,15] by means of high-

kinetic-energy photoelectron spectroscopy. Because of the much larger escape depth of high-kinetic-energy electrons our technique is a perfectly adapted tool to obtain information such that layer-resolved binary alloy composition profiles $A_{1-c}(n)B_c(n)$ at embedded A/B interfaces can be determined independently of any periodicity in the sample.

The shape of a photoelectron line from a particular core level will reflect the distribution of core-level binding energies of all A or B atoms in the sample. The peak position of this photoelectron line can thus be regarded as a measure of a characteristic core-level binding energy. The difference between the peak position from a bulk sample and the peak position from a multilayer sample may then be seen as the average core-level shift (CLS) of all A or B atoms in the multilayer. In order to reduce the complexity of the problem into a single characterization parameter which determines the main contribution to the core-level shift average we made the following assumptions about the interface roughness and structure of our samples: (i) the effects on the average core-level shifts from island structures at the interfaces in the sample are small; (ii) the main effect on the average core-level shift is due to intermixing of Cu and Ni atoms around the interfaces; and (iii) the spatial extent of the diffusion at an A/B interface may be described by a Gaussian distribution function with standard deviation Γ . This analysis has been successful in previous studies on magnetic properties [1] and makes a comparison between measurements and calculations realizable.

The layer-dependent concentration profile around one A/B interface is obtained as an integral over the Gaussian

distribution. The total concentration profile of the trilayer $A/B/A$ is then obtained as a sum over both A/B interface profiles in the model (for more details see Refs. [1,16]). The trilayer is the repeated unit in the experimental samples and constitutes the system that the calculation was performed on. Some examples of concentration profiles for a $\text{Ni}_5\text{Cu}_5\text{Ni}_5$ sample with different values of Γ are shown in Fig. 1. Given the number of atomic layers and the intermixing parameter Γ the average CLS of either the A or B atoms in the multilayer interface structure is determined within this model.

The challenge is to see if our technique is sensitive enough to analyze the details of the interface characteristics, which can be described in terms of variations in the interface roughness parameter Γ . We thus grew a set of three prototype multilayer systems, which were grown by UHV-based dc magnetron sputtering and include a stack of $\text{MgO}(001)/\text{Fe}_{5.6}/\text{Pt}_{39.2}/\text{Cu}_{45}/[\text{Ni}_{8.8}/\text{Cu}_N]_n/\text{Ni}_{8.8}/\text{Pt}_{10}$ (subscripts give the thickness in Å). The Cu thickness N was 5, 4, and 2 monolayers (9.0, 7.2, and 3.6 Å) while the number of bilayer repeats n was 15, 16, and 21, respectively. The Fe/Pt/Cu buffer [17] was grown at 150 °C, whereas the rest of the film was grown at room temperature. In the following we will refer to each sample according to the repeated trilayer unit of the multilayer as Ni_5Cu_N .

The samples were measured at the high-kinetic-energy (HIKE) station at the KMC-1 beam line [18] at BESSY, Germany. This beam line operates on a bending magnet and the x rays can be scanned in the range 1.7–12 keV. The HIKE end station is equipped with a Gamdata Scienta R-4000 hemispherical electron energy analyzer modified for high transmission and kinetic energy resolution up to 10 keV. The samples were studied using excitation energies of 2010 eV, where the overall resolution was determined to be 0.35 eV. The x-ray beam measurements were taken at grazing incidence, while the axis of the spectrometer lens was normal to the sample surface. We have estimated the inelastic mean free path to be in the range between 12–

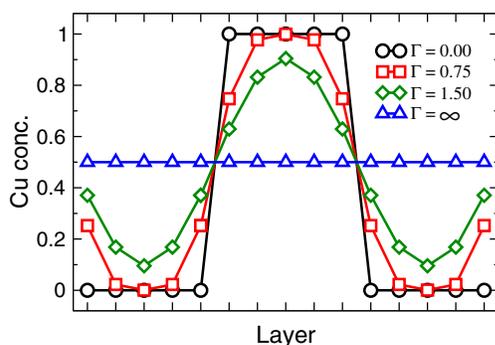


FIG. 1 (color online). Illustration of the Γ parameter for the case of $(\text{Ni}_5/\text{Cu}_5/\text{Ni}_5)_n$. Depending on the choice of Γ the concentration profiles have different spatial extent implying different degrees of intermixing.

20 Å in the materials Cu, Ni, and Pt for an excitation energy of 2 keV [19,20].

To control the interfacial quality of the multilayers, the samples were heated at a constant rate of 10 K/min up to a preset maximum temperature, held at that temperature for 5 min, and then subsequently cooled to room temperature, at which time the spectra were taken. Such Cu $2p_{3/2}$ photoelectron spectra were recorded for several temperatures in the range of 20–300 °C for all samples reflecting different amounts of interface intermixing.

For the theoretical part, all electronic structure calculations for the thin film nanomaterials were performed using an interface Green's function *ab initio* method [21–23]. In particular, we used a scalar relativistic density functional method where the alloying can be described within the coherent potential approximation [13].

The Cu/Ni multilayers in our calculations consist of a Cu layer embedded between two semi-infinite Ni crystals, which form a Ni/Cu/Ni trilayer sandwich. This setup allows us to calculate one repetition of Ni/Cu/Ni. Far away from the interface the electronic structure corresponds to that of bulk Ni. The geometry at the interface was not relaxed and the lattice structure of Ni was used throughout the trilayer except for the reference Cu core-level energy that was calculated in the lattice constant of pure Cu in order to replicate the experimental conditions. It is an approximation to not relax the interfaces and the detailed relaxation effects are not known. However, the lattice mismatch in Cu/Ni multilayers is small and chemical composition effects are assumed to be dominant.

The core-level shifts have been calculated in the complete screening picture, which includes both initial state (core-electron energy eigenvalue) and final state (energy relaxation) effects in the same scheme. Detailed descriptions of the complete screening method can be found in Refs. [13,24]. This method allows us to calculate the layer-dependent core-level shift profiles of a Ni/Cu_N/Ni system for any value of the interface intermixing parameter Γ . While low Γ values represent sharp interfaces in the $\Gamma \rightarrow \infty$ limit the system becomes a completely disordered random alloy.

We exemplify our x-ray photoemission data with the results obtained for the Ni_5Cu_5 system in Fig. 2, which is representative of all samples. A Cu $2p_{3/2}$ photoelectron spectrum obtained from a 200 nm thick Cu film grown on the same seed structure as the other samples is also plotted as a reference. We consider the thick Cu sample as bulklike and denote the spectrum as bulk.

The Ni_5Cu_5 sample has a small, but clearly observable positive chemical shift relative to the bulk Cu $2p_{3/2}$ photoelectron binding energy at room temperature. Upon heating to 150 °C no appreciable shift is seen. However, a closer inspection of the line profile reveals a distinct narrowing compared to the unheated case. Further heating to 200 °C does not shift the position of the peak maximum, but does give rise to an asymmetry of the line on the low

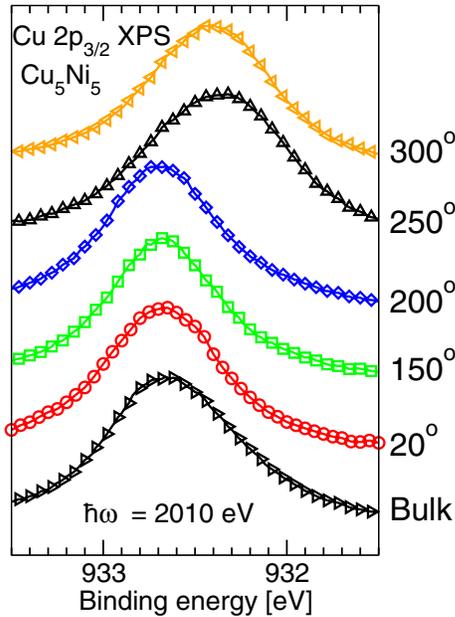


FIG. 2 (color online). The Cu $2p_{3/2}$ photoelectron spectra of the $(\text{Ni}_5/\text{Cu}_5/\text{Ni}_5)_n$ sample at excitation energy 2010 eV. Also included is a reference spectrum from a pure bulk Cu sample. As can be seen the destruction of the ordered multilayer structure is clearly observed as a chemical shift of the Cu $2p_{3/2}$ core-electron peak.

binding energy side. At 250 °C the peak maximum has clearly shifted towards a lower binding energy relative to the unheated value. Still further heating to 300 °C results in a small shift of the peak position, but in the opposite direction.

In Fig. 3 we show the energies of the peak positions and the full-width-at-half-maximum (FWHM) of the Gaussian contribution to the linewidths shown in Fig. 2, together with the calculated core-level shifts for some different interface diffusions. The representative data in Fig. 3, in fact, generally illustrate our interpretation of the results in Table I.

The FWHM is obtained by fitting the measured photoelectron lines with Voigt profiles with a fixed lifetime contribution to the total linewidths. The Gaussian contribution then reflects the distribution of core-level chemical shifts since the natural lifetime widths are not expected to vary much.

The small positive binding energy shift at room temperature is well described by the theory for an interface mixing with $\Gamma = 0.75$ or $\Gamma = 0.00$. After heating to 150 °C the FWHM clearly decreases. This, together with the relatively constant core-level shift, indicates that the annealing process results in a more homogeneous distribution of the atoms in the multilayers. At 250 °C the line becomes heavily broadened and the core-level shift now corresponds to the calculated value for a random alloy. Both the marked change in binding energy relative to the calculated value for a random alloy and the change in the

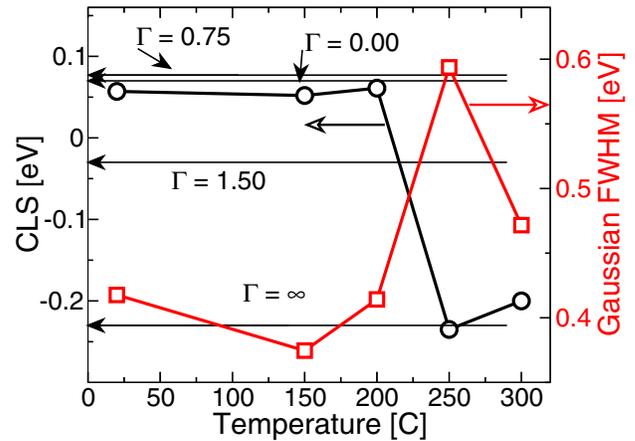


FIG. 3 (color online). The figure illustrates the chemical shift and the full width at half maximum of the Cu $2p_{3/2}$ core photoelectron spectrum for the $(\text{Ni}_5/\text{Cu}_5/\text{Ni}_5)_n$ sample and serves as a representative example of the results in Table I. The horizontal lines mark the calculated core-level shift obtained for different Γ and for the fully intermixed (dilute) situation. The agreement between experimental core-level shifts and calculated values is remarkable. As can be seen, the destruction of the ordered multilayer structure is clearly observed as a chemical shift of the Cu $2p_{3/2}$ core-electron peak as well as a clear change in linewidth.

spectral linewidth strongly suggest that the interface structure is destroyed, and the sample now is better described as a bulk alloy. Heating up to 300 °C results in a more homogeneous structure with more narrow photoelectron lines and a slightly changed core-level shift. Interestingly, the linewidth for the peak at 300 °C, as given in Fig. 3, is significantly more narrow than in the case of 250 °C for this sample. There may be several reasons for this behavior, but the analysis of this phenomenon goes beyond the scope of this Letter.

The sensitivity of the core-level shifts obtained by means of high-kinetic energy photoelectron spectroscopy for studies of this type is immediately evident from our results in Fig. 3 and Table I. For example, by matching the measured and calculated core-level shifts for the different samples in Table I we believe that the sample denoted Cu_2Ni_5 more likely consists of 3 ML Cu. This may be the case since the uncertainty in layer thickness determination from the x-ray diffraction analysis is typically ± 0.5 ML.

By comparing the measured peak positions at room temperature with the calculated core-level shifts for different Γ values in Table I we find that it is easy to identify different levels of interface intermixing in the multilayered materials. Generally, it is clear that all room temperature core-level shifts fit well to $\Gamma = 0.00$ if the Cu thickness of the Ni_5Cu_2 sample is assumed to be correct. However, an even better overall agreement is achieved if the Cu thickness in that sample is assumed to be 3 ML and the interface roughness $\Gamma = 0.75$. Since all samples were grown under

TABLE I. Summary of all results. The $\Gamma = \infty$ results correspond to completely random $\text{Cu}_{1-c}\text{Ni}_c$ alloys with concentrations according to the total content of Cu and Ni in each sample.

Sample	FWHM (eV)					CLS ^{exp} (eV)					CLS ^{theory} (eV)			
	20°	150°	200°	250°	300°	20°	150°	200°	250°	300°	$\Gamma = 0.00$	$\Gamma = 0.75$	$\Gamma = 1.50$	$\Gamma = \infty$
Ni ₅ Cu ₂	0.43	0.40	0.43	0.56	0.50	-0.06	-0.05	-0.06	-0.22	-0.23	-0.07	-0.15	-0.21	-0.20
Ni ₅ Cu ₃	-0.04	-0.05	-0.17	-0.20
Ni ₅ Cu ₄	0.44	0.40	0.44	0.60	0.59	0.00	0.03	0.01	-0.18	-0.19	0.07	0.02	-0.10	-0.21
Ni ₅ Cu ₅	0.42	0.37	0.41	0.59	0.47	0.06	0.05	0.06	-0.24	-0.20	0.07	0.08	-0.03	-0.23

identical conditions we assume that the degree of intermixing is the same for all three systems.

In conclusion, we have shown that it is possible to perform nondestructive studies of the quality of multilayer structures by using high-kinetic-energy electron spectroscopy, which, when combined with modern beam lines and electron analyzers, allows enough precision to follow the alloying of such nanolayered devices upon interface alteration. By comparing our measured core-level shifts to a detailed theoretical analysis, we have shown that the measurements can be understood qualitatively in terms of a modified interface roughness. The ability to vary the electron kinetic energy and hence the probing depth of our technique, furthermore allows for a depth profiling of the interface quality which is independent of interface periodicity.

Our results thus pave the way for a number of potential applications, such as monitoring aging effects in nanodevices or quantifying the quantum decoherence due to interface roughness. Other promising applications include interface roughness characterization of embedded clusters in semiconductor or metal hosts, as well as investigating boundaries between solid-liquid and liquid-gas phases.

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