# Reemitted-Positron Spectroscopy of Thin Metal Films

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Thin-film, bimetallic systems have been systematically investigated for the first time by means of reemitted-positron energy spectroscopy. Positron work functions for each layer, mean free paths, and thermalization rates can be directly observed. Interdiffusion alloying of a Cu film on Ni is observed. The technique, which is not affected by surface contamination, is highly sensitive as a materials probe of processes that affect the bulk chemical-potential-energy sum, $\mu^+ + \mu^-$.

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There is a great deal of interest in the fundamental physics and technical applications of thin metal films deposited on metal substrates. The tremendous variety of overlayer-substrate combinations facilitates investigations of nucleation and growth, interdiffusion processes, phase transitions, surface and thin-film electronic structure, surface catalysis, etc. under systematically controlled conditions. Such thin-film systems are also ideal for probing the interactions of low-energy positrons ($E \simeq 1$ eV) with bulk matter and interfaces.[1] The fact that positrons which have been implanted into a multiple-layer system can be spontaneously reemitted (under certain conditions) with well-defined energies characteristic of each material in the structure provides the basis of reemitted-positron spectroscopy (RPS) as a new probe of thin metal films.

The energy spectrum of positrons reemitted from single-crystal surfaces has been recently investigated.[1-6] High-resolution studies[3-5] show that there is a narrow peak ($\simeq 75$ meV FWHM at 300 K) corresponding to positrons elastically emitted with kinetic energy $-\phi^+$, provided the positron work function $\phi^+$ is negative. A tail of inelastically scattered positrons which extends down in energy until it abruptly cuts off defines zero positron energy. (Thus the energy difference between the zero cutoff and the elastic peak is equal to $\phi^+$.) The influences of adsorbates,[1-3] energy-loss process,[3,4,6] and interfacial defects[1] on the positron reemission have been studied.

A complete description of positron diffusion in, and emission from, thin films and substrates will require knowledge of the positron energy level in each component, the positron implantation depth profile, and detailed considerations of hot-positron transport (mean free paths, energy-loss processes, defect trapping, etc.) in the films and at interfaces. In this Letter we will concentrate on the basic, material-specific, spectroscopic features of RPS, specifically the positron energy levels in each layer and the elastic mean free paths of hot positrons ($E \simeq 1$ eV) penetrating through an overlayer. We will present experimental results of the first systematic investigation of thin-film, bimetallic systems [Cu on Ni(110), Ni on Cu(111), Cu on Co(0001), Au on Ni(100), and Au on Cu(111)] using RPS. The high sensitivity of RPS to certain bulk properties, without sensitivity to surface contamination, will be demonstrated.

The experimental arrangement we use for measuring reemitted-positron energies is very similar to that used in photoemission spectroscopy. A commercial, double-pass, cylindrical mirror electron energy analyzer (PHI model 15-255G) is electrically modified[7] to analyze positively charged particles in a constant pass-energy mode. A variable-energy (1–8 keV) positron beam enters the chamber perpendicular to the analyzer axis and implants positrons in a 1-mm-diam beam spot on a target oriented $\simeq 42°$ from this axis. At these energies, the positrons are implanted[8] up to a depth of order several hundred angstroms. With the pass energy held constant at $\simeq 7$ eV the voltage on the preacceleration grids is stepped (30 meV/step) under computer control over a 2–4-V range while a counter records the detected transmitted positron rate (200–300 cps on the peak) through the analyzer. The angular acceptance of the analyzer is $\pm 6°$ and the energy resolution is 150 meV under high-transmission conditions.[7] The total yield of reemitted positrons ($\simeq 4000$ cps detected) is measured separately with a simple, biased, electron multiplier arrangement.

In a multilayer structure, charge transfer across the junctions equalizes the electron Fermi levels of the various layers. There is no corresponding equalization of positron "Fermi levels" (ground-state energy levels) and thus each layer will have a distinct value of $\phi^+$. The previous work on RPS[1-6] and positronium emission[9] can be extended to include a system of any number of layers. The electron distribution gives rise to interface dipole potential differences at the metal-metal junctions so that $\phi_i^-$ of any layer is just $\phi_1^-$, the electron work function of the top layer. The positron work function of the $i$th layer is

$$\phi_{i'}^+ = (\phi_i^+ + \phi_i^-) - \phi_1^-, \tag{1}$$

where $\phi_i^+$ and $\phi_i^-$ are the respective work-function values for a clean surface. The energy measured as the elastic peak in the analyzer, $E_i^+ = -\phi_{i'}^+$, is modified

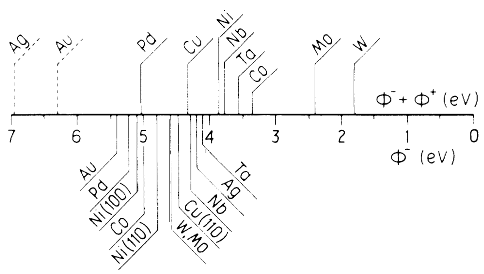


FIG. 1. Measured reemitted-positron elastic peak energies (top), and top-layer electron work functions (bottom, from Ref. 10) which correspond to zero cutoffs in RPS. Reverse scales for $\phi^+ + \phi^-$ are used so that the reemitted energy increases to the right. All peak energies are measured relative to the Ni peak, and the absolute scale is set by the assumption that the observed Ni(100) zero cutoff corresponds to $\phi^- = 5.1$ eV (Ref. 10). The Ag and Au peaks are theoretical prediction. (Ref. 11).

by the sample-analyzer contact potential difference $\phi_A^- - \phi_I^-$ (see also Refs. 1-3). Using Eq. (1), we have

$$E_i^+ = -(\phi_i^+ + \phi_i^-) + \phi_A^- . \quad (2)$$

Since the bracketed quantity depends only on the bulk chemical potentials of the layer [i.e., $-(\phi_i^+ + \phi_i^-) = \mu_i^+ + \mu_i^-$], and provided $\phi_A^-$ is a constant, the RPS elastic peak of this material is independent of the presence of any overlayers. This effect[1] (and similar effects for surface contamination[2-5]) has been observed. The change in $\phi^+$ [given by Eq. (1)] is observed as a shift in the zero cutoff. Figure 1 shows some measured peak energies (see references for others). With reference to Fig. 1 and Eqs. (1) and (2), the features of a RPS spectrum of a multiple-layer structure can be summarized as follows: (1) The elastic peak position is invariant and depends on the bulk chemical potentials $\mu^+ + \mu^- = -(\phi^+ + \phi^-)$. (2) The zero cutoff is determined by $\phi^-$ of the system, that is $\phi^-$ of the top layer. (3) The change in $\phi^+$ of a given layer as additional layers are deposited is the negative of the change in $\phi^-$. (4) Thermalized positrons in a particular layer are energetically forbidden from entering any adjacent layer if the peak for that layer is located to the right in Fig. 1. If the peak of an overlayer is to the left, a positron crossing the interface will initially have excess energy corresponding to the difference in peak energies. (5) A peak from a layer will actually appear in a spectrum if all the overlayer peaks are located to the left *and* if the zero cutoff is also located to the left.

We first studied the systems Cu on Ni(110) and Ni on Cu(111). In Fig. 2, the evolution of the RPS spectrum is shown as Cu is successively evaporated up to a thickness of $\simeq 118$ Å on Ni(110) at room temperature. The Cu evaporation rate of 1-2 Å/min was calibrated by Auger spectroscopy. During evaporation the chamber pressure remained below $5\times10^{-10}$ Torr and ordered growth of the overlayer was confirmed with LEED. As

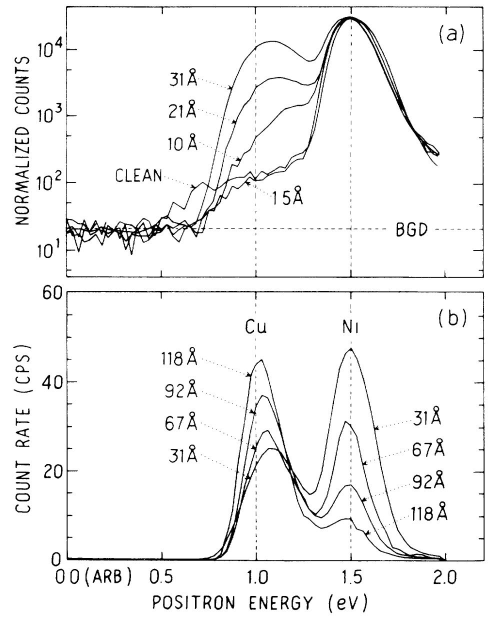


FIG. 2. Reemitted-positron energy spectra, acquired at 4-keV incident beam energy, for various thicknesses of Cu on Ni(110). Spectra have been normalized in (a) to peak height and in (b) to total beam rate. Note the logarithmic scale for (a).

expected from point (2), the clean Ni(110) zero cutoff is shifted by 0.3 eV from that for Ni(100), and it shifts by an additional 0.3 eV [see Fig. 2(a)] when Cu(110) is grown epitaxially on top, these results being consistent with existing values[10] of $\phi^-$. Consistent with point (5), two peaks are observed in Fig. 2(b) (see also Ref. 1). Up to the maximum Cu thickness of 118 Å, the Ni peak location is observed to be invariant, as expected from point (1). This result was found to be universal—i.e., independent of surface orientation of the sample [Ni(110) vs Ni(100)], surface contamination (S, C, O, CO, Cd, Zn), and overlayer composition (Cu, Au). Since *relative* measurements (as in Fig. 1) of peak positions can probably be made at the 10-meV level or better, this should pose a significant challenge for theoretical calculations of $\mu^+ + \mu^-$.

The Ni substrate peak rate decreases with Cu overlayer thickness, $x$, as shown in Fig. 3, with a concomitant increase in a "mound" of inelastically scattered positrons [see Fig. 2(a)]. The persistence of the Ni peak in the spectrum is not due to islanding since the Ni Auger peaks disappeared at $x = 40$-$50$ Å in a manner consistent with layer-by-layer growth. It is, instead, due to the long mean free path, λ, of 0.5-eV positrons (i.e., the Cu-Ni peak energy difference) in metals.[12] We interpret the roughly exponential drop in Fig. 3 as a direct measure of a quasielastic mean free path, λ, since virtually any scattering event should produce either sufficient energy loss or sufficient angular deflection to remove the posi-

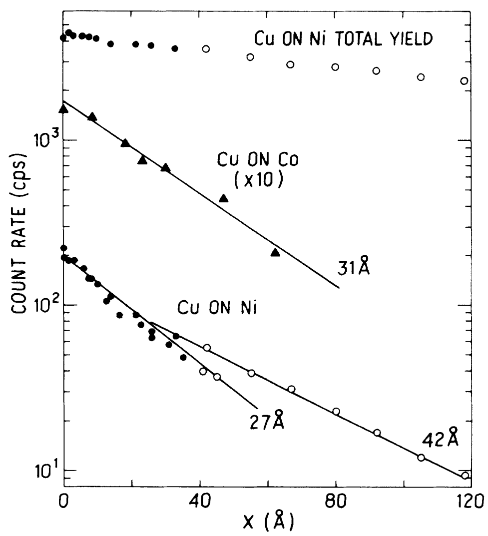


FIG. 3. The substrate peak counting rate and the total reemitted-positron rate vs Cu overlayer thickness, $x$. The open symbols denote runs where $x$ is estimated (since the substrate Auger line is no longer observable).

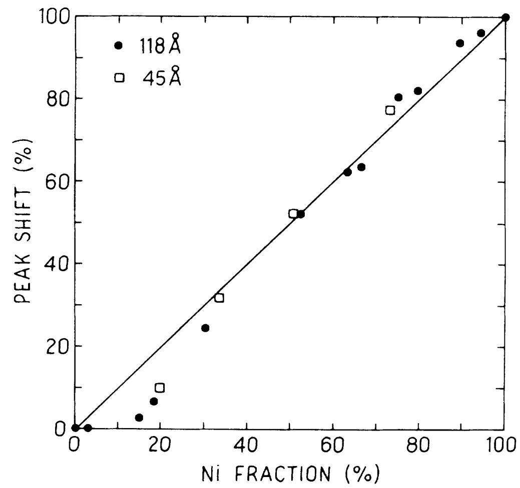


FIG. 4. The elastic-peak energy shift from that of a pure Cu film on Ni(110) to that of pure Ni is shown vs the film's Ni alloy fraction (as determined by Auger analysis). The straight line is for reference. No correction for Cu surface segregation was made in the Auger analysis, and the small shift at low Ni fraction is probably due to Ni grain-boundary diffusion to the surface without bulk interdiffusion.

tron from the peak counting rate. Neglecting the small decrease in the number of positrons which are implanted in the substrate due to loss of incident positrons in the overlayer, we find $\lambda$ to be about 30–35 Å for 0.5-eV positrons in Cu. (The average range of 4-keV positrons in Cu is around 300 Å.[8]) We find very nearly the same result for the 1-eV positrons in Cu from a Co(0001) substrate (Fig. 3). A calculation[12] of $\lambda$ which includes both electron-hole pair production and phonon scattering indicates that $\lambda(1\text{ eV}) \approx \lambda(0.5\text{ eV}) \approx 40$ Å at room temperature in Al. (It would be interesting to have calculations specifically for Cu.) The calculation also predicts a strong dependence of $\lambda$ on temperature for energies less than several electronvolts, a prediction we should be able to test in the future.

The inelastic mound in Fig. 2(a) gradually forms the Cu peak in Fig. 2(b), but the correct peak energy is only roughly attained by $x=118$ Å and the peak FWHM is too broad by several times $kT$ ($kT \simeq 25$ meV). Given $\lambda(0.5\text{ eV}) \approx 30$–$40$ Å, it is understandable that at least 100 Å of Cu overlayer is required to thermalize the hot positrons from the Ni substrate. Calculations[12] of positron thermalization rates (again for Al) predict that positrons will diffuse $\simeq 100$ Å before reaching thermal energies, in qualitative agreement with our observation. High-resolution RPS would be able to investigate thermalization rates rigorously by measurement of peak width as well as the peak energy. With the wide variety of thin-film–substrate combinations available, it should be possible to test accurately calculations of temperature-dependent positron mean free paths and thermalization rates in many materials in an energy regime where no direct measurements exist.[6]

The results of the evaporation of Ni on Cu(111) and Au on Ni(100) and Cu(111) are intriguing. As expected from point (4), we find that the Cu substrate peak rate and total positron yield drop rapidly to zero with only 15 Å of Ni evaporated on it. Clearly the more negative work-function material (Ni) presents a barrier for positrons thermalized in the Cu. Conversely, evaporation of a Au overlayer, which alone has positive $\phi^+$, does not cut off reemission. For Au on Cu(111), total reemission actually increased by up to 30% for $x < 10$ Å. Similar to the effect of S on Cu,[2] Au makes the Cu positron work function more negative, thus enhancing reemission. For thicker layers, the Au becomes a one-dimensional positron trap and the reemitted rates decreased steadily as inelastic scattering reduced the positrons' energies in the Au below the zero cutoff.

The potential of RPS as a materials probe can be seen in two effects, alloying and temperature changes, that produce shifts in the elastic peak position. Interdiffusion alloying of the Cu film on Ni(110) was observed by our annealing samples with 45- and 118-Å thick Cu films for 2 min at successively higher temperatures, $T_A$. The Ni RPS peak disappears by 400 °C while the Ni *Auger* peaks reappear at $T_A \gtrsim 440$ °C! At higher $T_A$, the single remaining peak in the RPS spectrum shifts continuously (as shown in Fig. 4) from the Cu location to the Ni peak location ($T_A = 930$ °C and no Cu in the Auger spectrum). It is known that rapid interdiffusion of Cu-Ni films occurs above 400 °C and that the Ni-in-Cu diffusion rate is 10–30 times the Cu-in-Ni rate.[13] We attribute the existence of a single, narrow "alloy" peak in the spectrum to rapid diffusion of Ni into the Cu producing a relatively homogenous Cu-Ni alloy layer. The shifting of the alloy peak is a manifestation of an effective chemical-potential sum $(\mu^+ + \mu^-)$ of the alloy overlayer that is intermediate between the values for Cu and Ni. Calculations of $\mu^+ + \mu^-$ for alloys would be thus of immediate interest. RPS is evidently quite sensitive to such compositional changes (at least for metals with $r_s \sim 2$) since the quantity $\phi^+ + \phi^-$ ranges over 5 eV (see Fig. 1) while $\phi^-$ changes by only $\simeq 1.3$ eV.

Consistent with previous measurements[2-5,9,14] we observe strong temperature-dependent shifts in the elastic peak position [e.g., $-0.77 \pm 0.02$ meV/°C for Cu with $50\,°C < T < 350\,°C$.] These shifts are interpreted[14] as mainly due to volume expansion on heating and a positron deformation potential of order 10–15 eV can be deduced[14] and compared with theory.[15] With 0.01-eV sensitivity, RPS would then be sensitive to 0.1% volume dilatations and thus could be useful in probing lattice strain induced, for example, by external stress or by misfit stress encountered in pseudomorphic film growth (we are presently pursuing this latter application of RPS).

Finally, we note that measurements[9] of the *positronium* work function $\phi^{Ps} = \phi^+ + \phi^- - 6.8$ eV are, by comparison with Eq. (1), sensitive to the same quantities as RPS. In fact, $\phi^{Ps}$ can be determined with RPS by subtraction of 6.8 eV from the peaks in Fig. 1. Conversely, measurements of $\phi^{Ps}$ and $\phi^-$ on metals with large positive values of $\phi^+$ that are not directly accessible to RPS (e.g., Au, Ag, Pb) could be used to determine their peak positions in Fig. 1. Both techniques, although very different in practice, share the great advantage that surface contamination does not disrupt the measurements[9] as it does for $\phi^-$-based techniques.[10] Thus, the combination of high sensitivity to bulk effects (alloying, volume deformations), insensitivity to surface preparation, and a relatively simple analysis technique with a standard energy analyzer should make reemitted-positron spectroscopy an attractive probe of material properties.

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