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Temperature dependence of low-energy positron-induced Auger-electron emission: Evidence for high surface sensitivity

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We report the experimental observation of the temperature dependence of the intensity of low-energy positron-annihilation-induced Auger-electron emission spectroscopy (PAES) from Cu(100). These studies show that the mechanism for stimulating Auger electrons is found to compete with positronium (Ps) emission from a surface. The positrons that induce Auger-electron emission therefore originate from the same surface state from which Ps is thermally desorbed. Hence, PAES should have higher surface sensitivity (~1 Å) relative to conventional methods for generating Auger-electron emission from surfaces (~5–10 Å).

The energy distribution of Auger-electron emission from a solid is often used to determine the elemental composition of the surface region.[1] Conventional Auger-electron spectroscopic techniques initiate the Auger emission process by generating core holes through collisional excitations of energetic electrons, protons, x rays, etc. Recently, experiments have demonstrated that the annihilation of low-energy positrons (~30 eV) can also stimulate Auger-electron emission[2,3] from surfaces. During this process, positrons with energies well below the core-level ionization threshold are implanted into a material, slow down through a variety of inelastic processes, and diffuse back to the surface region. There, the positron may annihilate with a core electron and create a core hole which results in the emission of an Auger electron. Such a process has intrinsic interest but may also be valuable as a new surface spectroscopic technique, specifically, positron-induced Auger-electron spectroscopy (PAES).

This paper discusses the first study of the temperature dependence of the positron-annihilation-induced Auger-electron intensity. The Auger-electron emission intensity in this study is found to be a strong function of temperature especially near 400 °C for Cu(100). In contrast, the Auger-electron intensity generated by collisional excitations is experimentally observed to be temperature independent.[1] This study finds that the temperature dependence of the PAES intensity arises from the competition between the annihilation process and "thermal" positronium formation.[4,5] In this paper, we demonstrate that the positron that induces the Auger-electron signal originates not from a subsurface defect, but instead from the same surface state from which positronium is thermally desorbed. Hence, PAES should provide information on the elemental composition much closer to the surface (~1 Å) relative to conventional Auger-electron emission techniques (~5–10 Å), which are determined by the escape length of the Auger electron. Any model of thermal positronium emission must also be consistent with the PAES intensity.

The measurements reported in this paper were performed using a system (described previously[6]) consisting of a magnetically guided positron beam and a trochoidal spectrometer[7,8] which was recently constructed at Brookhaven National Laboratory. The beam used a solid neon moderator coated[9] onto a cooled 0.4 mCi Na^{22} positron source. Three sets of $\mathbf{E}\times\mathbf{B}$ plates, shown in Fig. 1, were used to direct the low-energy positrons (30 eV) onto a Cu(100) target and collect the Auger electrons. The second and third $\mathbf{E}\times\mathbf{B}$ plates were used as energy dispersive elements so that the distance an electron is deflected after emerging from the target is proportional to $E^{-0.5}$ (E is the kinetic energy). A one-dimensional position-sensitive detector (1D PSD) measured the deflection of the electrons and, hence, their kinetic energy. Parallel collection of the energy spectrum permitted rapid data acquisition in spite of the low incident positron beam rates. The position spectrum was related to an energy

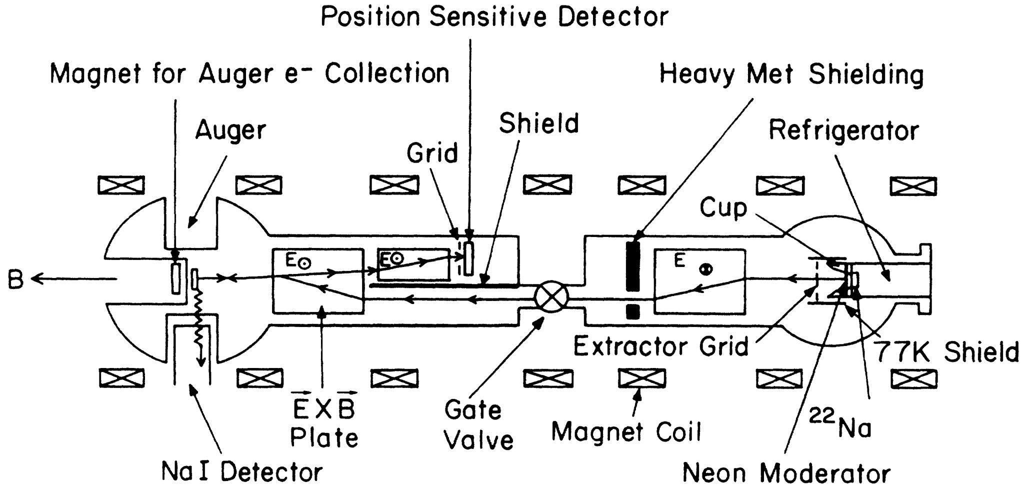

FIG. 1. Schematic drawing of apparatus showing source, refrigerator, **E**×**B** plates, target, 1D PSD, NaI γ-ray detector.

scale by comparing the position of positron-induced secondary-electron emission from the copper target biased to various voltages and subsequently checked with a retarding grid located in front of the 1D PSD. In addition, a NaI detector located near the sample monitored the γ-ray spectrum from the sample which (1) monitored the positronium fraction by comparing the background to the annihilation peak,[4] (2) provided a signal for the incident positron beam intensity actually hitting the sample, and (3) provided a gate signal for the coincidence spectrum of the 1D PSD and helped identify the PAES signal. The Cu(100) sample was cleaned by Argon sputtering and its surface composition was checked using conventional Auger-electron techniques and the oxygen and carbon contamination remained less than 1 and 3 %, respectively, during the course of the measurements. Before insertion into the experimental chamber, the Cu(100) had been heated to 600 °C in a flowing H/Ar atmosphere for 48 h in order to eliminate sulphur contaminants from the bulk and avoid sulphur migration to the surface during sample heating.

Figure 2 shows a gated position spectrum from the 1D PSD for electrons emerging from a Cu(100) crystal at room temperature and 700 °C due to positrons hitting the sample with 32 eV. The gate is generated from the NaI scintillator γ-ray detector windowed around the 511-keV peak. Gating the signal ensured that features in the energy spectrum were associated with the annihilation of a positron at the target and eliminated background effects and detector artifacts. The sample was biased to -2 V to attract the slow reemitted positrons back to the sample. The broad peak in the high-channel-number region (corresponding to the $M_{23}VV$ transition in copper and $\sim$60-eV kinetic energy as checked with secondary electrons) is the PAES signal of interest in the present study. The width of the peak reflects the broad energy resolution due to the large diameter of the present positron beam. It should be noted that the low-temperature sample has substantially more counts in the PAES part of the spectrum in Fig. 2 relative to the high-temperature sample which indicates a reduction of Auger-electron emission at elevated temperatures.

Figure 3(a) shows the integrated PAES intensity of the peak (after correction for background and random coincidences) as a function of temperature of the sample. Each point in Fig. 3(a) corresponds to a measuring time of 15 min. The data was collected at various sample temperatures while the sample was heated from room temperature to 700 °C, cooled to 200 °C, and then reheated to 800 °C. This procedure was used to ensure that the measurements were taken from clean samples and to check for systematic errors. The intensity of the peak decreases as the sample temperature is increased as depicted in Fig. 2. Also shown in Fig. 3(a) is the temperature dependence

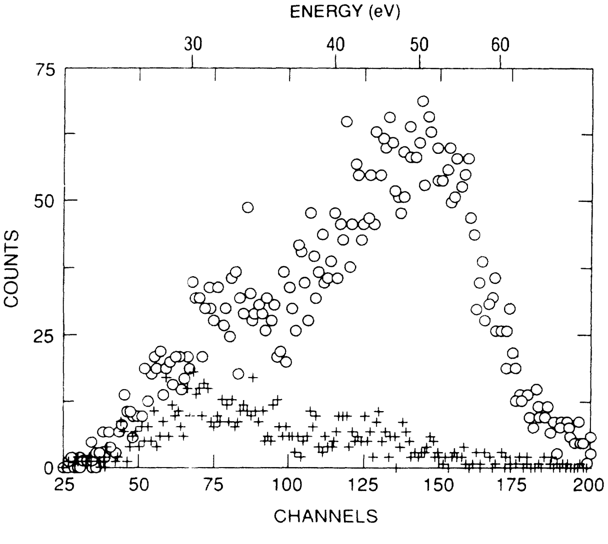

FIG. 2. Energy spectrum of electrons emitted from Cu(100) for room temperature (△) and 700° C (+). Spectra from 1D PSD gated by annihilation γ rays from target. Incident positron beam energy is 30 eV. The abscissa is the deflection of channel number and corresponds to increasing electron kinetic energy. The PAES feature occurs at high-channel number or $\sim$60 eV energy. Note suppression of PAES feature at 700 °C.

of $1-f$, where f is the relative fraction of positronium formation found in Ref. 4 for 70-eV positrons hitting a Cu(100) surface and therefore $1-f$ is the total fraction of positron annihilations f_A with the sample. (The difference in positronium formation for 30 and 70-eV positrons should be small.[10]) To facilitate the comparison of the PAES intensity with positronium emission, the PAES and $1-f$ intensity spectra have been scaled to match at 200 °C. As can be seen in Fig. 3(a), there is good agreement in the two sets of curves although there is a small divergence at higher temperatures. In addition, the relative positronium fraction was determined during the PAES measurements by taking the ratio of the peak-to-background counts in the annihilation γ-ray energy spectrum in the NaI detector or ("$2\gamma/3\gamma$") method[4] where the values for positronium formation at 30 and 800 °C were matched to those of Mills.[5] All the values for positronium formation obtained during the PAES measurements are shown in Fig. 3(b) and closely follow the values from the earlier work.[5]

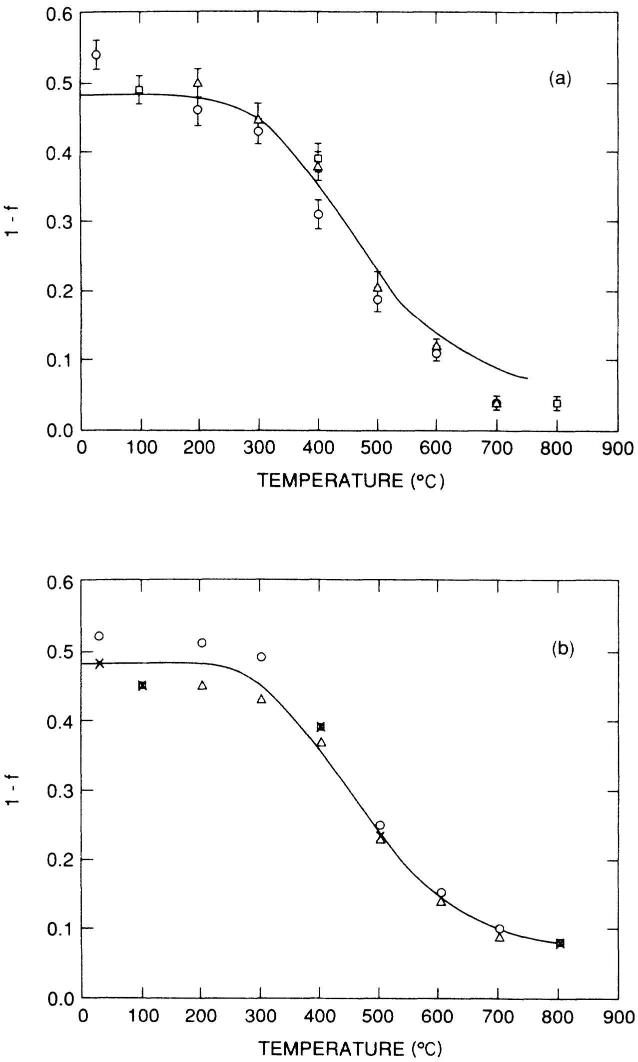

FIG. 3. (a) Temperature dependence of PAES from Cu(100). First ramp up from room temperature to 700 °C (○), ramp down in temperature (△), and finally ramp up to 800 °C (□). Due to rescaling of PAES data to thermal positronium, the vertical axis for the PAES data is in arbitrary units. Also shown is $1-f$ where f is the positronium fraction from Mills (solid line). (b) Temperature dependence of positronium formation using the peak to total annihilation γ-ray spectra and compared to $1-f$ and f is taken from a previous measurement of Mills. Same temperature cycle and markers are used as in (a) except (×) denotes a final ramp down in temperature. Statistical error bars are the size of the circles in the figure.

The correlation of the temperature dependence of PAES with $1-f$ as shown in Figs. 3(a) and 3(b) demonstrates that the process leading to the PAES signal directly competes with thermal positronium formation. The connection between PAES and f can be understood in terms of a model (for positrons implanted in a negatively biased sample to prevent positron reemission) in which the positron either annihilates in a surface state (with probability f_A) or leaves the surface with an electron forming positronium (with a probability f). For those positrons returning and getting trapped in a surface state, the relationship between the relative probabilities is summarized in Eq. (1):

$$1=f_A+f\ . \qquad (1)$$

If the fraction $f_{\rm Aug}$ of positrons that annihilate at the surface and result in Auger-electron emission is temperature independent, then the temperature (T) dependence of the positron-induced Auger-electron intensity $I_{\rm Aug}(T)$ follows:

$$I_{\rm Aug}(T)\propto f_{\rm Aug}f_A \propto 1-f\ . \qquad (2)$$

The assumption that $f_{\rm Aug}$ is temperature independent is reasonable since the thermally induced expansion and relaxation of the top surface layer of a few percent should not significantly affect the overlap of the positron and core-electron wave functions and consequently not alter the Auger-electron intensity. Figure 3(a), in which PAES intensities are plotted on the same graph as $1-f$, with f taken from Ref. 5, clearly indicates that most of the PAES signal can be accounted for through expression (2). Above ~500 °C the measured PAES intensities are lower than the values predicted using the values f measured previously.[5] Alternatively the PAES intensity could be used to determine the positronium fraction. A better fit to the data can be obtained by assuming that the positronium fraction is 95% at 800 °C rather than 90% as previously found.[5] The difference between these two values is well within the 10% systematic errors quoted in Ref. 5.

The idea that PAES and thermal positronium are competitive processes and therefore have identical origins has several implications for the surface sensitivity of PAES and the nature of the source of thermal positronium. Extensive calculations found that thermal positronium can only originate from regions of reduced electron density such as surface states in a defect-free metal[11] and that a positron can be bound by an image-correlation potential[12] to a region confined to within ~1 Å of a surface. These ideas were confirmed experimentally in lifetime studies[13] and the observed sensitivity of positronium emission from metals[4,5] to both temperature and the presence of adsorbates on a surface. The present study on the relationship between PAES and positronium along with the earlier work on thermal positronium emission therefore imply that the PAES signal itself originates from a region confined to within ~1 Å of the surface. Surface sensitivity of Auger-electron emission using conventional methods is determined by the escape length of the Auger electron (5–10 Å) and is therefore much less surface sensitive than PAES. Support for these ideas was observed in the strong dependence of the PAES intensity on surface impurities.[3] Similar to some theories on thermal positronium emission, experimental PAES intensities can be understood in terms of a model in which a positron sits in a delocalized two-dimensional surface state[3,14] prior to annihilation with a core electron. Any model of thermal positronium emission must also be able to account for the PAES intensity and therefore a new constraint is imposed on theories of positron interactions with metals.

The highly surface localized nature of the PAES signal may complement conventional Auger-electron emission studies. The relatively large penetration depth of electrons or photons used in conventional techniques requires the consideration of the contributions to the Auger signal from the bulk. This is even true when using the highly sensitive surface technique[15] of gating the Auger electron signal with the surface photoelectron. In addition, the positron is spin polarized[16] and it is therefore possible to form a spin-polarized core hole due to the strong dependence of the annihilation process on the relative spin orientation of the positron and core electron. The probability of Auger-electron emission should then depend on the relative spin orientation of the valence electron (if it is involved in filling the core hole) and the core electron.[17,18] Implanting a polarized positron beam into ferromagnetic target and using high-energy-resolution PAES should provide a sensitive probe of surface magnetism.

In summary, we have experimentally observed a temperature dependence for the low-energy positron-induced Auger-electron emission from a clean metallic surface. Further, the temperature dependence of the positron-annihilation-stimulated Auger-electron process suggests that this mechanism competes with thermal positronium emission. This can be understood in terms of a model in which the positron residing in the same surface state as the one associated with positronium emission annihilates with a core electron and results in the emission of an Auger electron. These experimental observations provide strong evidence of the higher surface sensitivity for positron-annihilation-stimulated Auger-electron emission relative to those initiated by collisional processes.

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