Theoretical aspects of studies of oxide and semiconductor surfaces using low energy positrons

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Abstract. This paper presents the results of a theoretical study of positron surface and bulk states and annihilation characteristics of surface trapped positrons at the oxidized Cu(100) single crystal and at both As- and Ga-rich reconstructed GaAs(100) surfaces. The variations in atomic structure and chemical composition of the topmost layers of the surfaces associated with oxidation and reconstructions and the charge redistribution at the surfaces are found to affect localization and spatial extent of the positron surface-state wave functions. The computed positron binding energy, work function, and annihilation characteristics reveal their sensitivity to charge transfer effects, atomic structure and chemical composition of the topmost layers of the surfaces. Theoretical positron annihilation probabilities with relevant core electrons computed for the oxidized Cu(100) surface and the As- and Ga-rich reconstructed GaAs(100) surfaces are compared with experimental ones estimated from the positron annihilation induced Auger peak intensities measured from these surfaces.

1. Introduction

Oxide and semiconductor surfaces play a fundamental role in modern science and technology. Unlike conventional Auger techniques that average over several atomic layers, positron annihilation induced Auger electron spectroscopy (PAES) has a very high degree of top layer selectivity due to the fact that the positrons are trapped just outside the surface prior to annihilation, hence is ideal to probe the near surface region \cite{1}. Recently this technique has been applied to study the oxidized Cu(100) single crystal to gain a better understanding of the corrosive and catalytic processes associated with thin film metal oxides and the GaAs(100) surface that exhibits a variety of surface reconstructions, roughly classified as As-rich and Ga-rich phases \cite{2}. The experimental annihilation probability, $p_{nl}$, of surface trapped positrons with Cu $3p$ core electrons estimated from the measured intensity of the positron annihilation induced Cu $M_{2,3}VV$ Auger peak shows a large increase as the oxidized Cu(100) single crystal is subjected to a series of isochronal anneals in vacuum up to annealing temperature 300 °C, which then decreases monotonically as the annealing temperature is increased to ~550 °C \cite{3}. The PAES spectrum from GaAs(100) displays six As and three Ga Auger peaks corresponding to $M_{4,5}VV$, $M_2M_4V$, $M_{2,3}M_{4,5}$ Auger transitions for As and $M_{2,3}M_{4,5}M_{4,5}$ Auger transitions for Ga. Experimental positron annihilation probabilities $p_{nl}$ with As $3p$, $3d$, and Ga $3p$ core electrons estimated from the Auger peak intensities are equal to 0.51%, 0.92%, and 0.33%, respectively \cite{4}. The experimental positron work function, $\Phi_p$, is equal to -0.6±0.1 eV \cite{4}. Because of the variety of reconstructions of the GaAs(100) surface, positron annihilation probabilities are expected to be affected by atomic structure and elemental composition of the topmost layers of the surface \cite{5}.

This paper presents the results of theoretical studies of positron surface states and annihilation characteristics of surface trapped positrons with relevant core electrons at the oxidized Cu(100) surface and at both As-rich and Ga-rich reconstructed GaAs(100) surfaces. Such studies are indispensable for clarifying localization and spatial extent of the positron surface-state wave function at oxide and semiconductor surfaces, and the surface atomic structure and chemical composition dependence of probabilities of annihilation of surface-trapped positrons with relevant core-level electrons, the information needed to explain the experimental PAES data.
2. Theory

The positron potential $V(r)$ at a semiconductor surface contains an electrostatic Hartree potential $V_{H}(r)$ and a correlation part $V_{\text{corr}}(r)$. $V_{H}(r)$ is constructed as a superposition of atomic Coulomb potentials. Atomic calculations were performed self-consistently within the local-spin-density approximation [6] using the exchange-correlation functional from Ref. [7]. We followed the method of Weinert and Watson [8] to account for the effects of charge redistribution at the surface and placed the atoms in a "compensating" potential well extending from the atom center out to one Wigner-Seitz radius and then linearly ramping to a value of 0.00 Ry at twice the Wigner-Seitz radius and beyond. The atomic wave functions then provided the overlapping electron densities and corresponding atomic Coulomb potentials via Poisson's equation.

$V_{\text{corr}}(r)$ is described in the bulk using the local density approximation (LDA) [5, 9]. Outside the surface $V_{\text{corr}}(r)$ is described by the image-type potential that is constructed to have the same corrugations as the total electron density [5, 10]. Positron surface states were obtained by solving Schrödinger’s equation numerically with the boundary condition that the positron wave function vanishes sufficiently far into the bulk or the vacuum. Positron annihilation rates, $\lambda_{n,l}$, with specific core electrons, described by quantum numbers $n$ and $l$, and the total annihilation rate, $\lambda$, (and corresponding positron surface state lifetime, $\tau$) are calculated taking electron-positron correlation effects explicitly into account using the LDA [5, 9]. The probability of annihilation of surface trapped positrons, $p_{n,l}$, with electrons in the core level $n,l$ is obtained dividing $\lambda_{n,l}$ by $\lambda$: $p_{n,l} = \lambda_{n,l} / \lambda$.

3. Results and discussion

Calculations of positron surface states and annihilation probabilities of surface trapped positrons with relevant core electrons, $p_{n,l}$, were performed for the oxygen adsorption at surface hollow sites of the unreconstructed Cu(100) surface. We considered 1/8, 1/4, 1/2 and one monolayer (ML) oxygen coverages. Calculations were also performed for the missing row (MR) reconstructed Cu(100) surface with 0.5 ML on-surface and 0.5 ML sub-surface oxygen coverages. In the latter case the adsorbed O atoms occupy surface hollow and subsurface octahedral sites. All surfaces were fully relaxed in calculations. The computed binding energy, $E_{b}$, for a positron trapped at the oxidized Cu(100) surface, the positron surface-state lifetime, $\tau$, and the annihilation probabilities of the surface trapped positron with relevant core electrons, $p_{n,l}$, are given in Table 1.

Table 1. Theoretical positron binding energy, $E_{b}$, positron surface-state lifetime, $\tau$, annihilation probabilities of the surface trapped positron with relevant core electrons, $p_{n,l}$, computed for the oxidized Cu(100) surface.

| System                        | $E_{b}$ (eV) (theory) | $\tau$ (ps) surface state (theory) | Cu 3s | Cu 2p | Cu 2s+2p | O 1s |
|-------------------------------|-----------------------|------------------------------------|-------|-------|---------|------|
| Cu(100)                       | 2.75                  | 461                                | 1.766 | 6.990 | 8.756   |      |
| Cu(100) + O (1/8 ML)          | 3.14                  | 503                                | 1.203 | 4.806 | 6.009   | 0.030|
| Cu(100) + O (1/4 ML)          | 3.12                  | 495                                | 1.043 | 4.172 | 5.215   | 0.067|
| Cu(100) + O (1/2 ML)          | 3.08                  | 470                                | 0.748 | 2.991 | 3.740   | 0.142|
| Cu(100) + O (1 ML)            | 2.94                  | 448                                | 0.398 | 1.595 | 1.993   | 0.227|
| Cu(100)+O (0.5 ML on-surf. +0.5 ML sub-surf.) | 3.02 | 394 | 0.322 | 1.406 | 1.728 | 0.089 |

It follows from Table 1 that $E_{b}$, $\tau$, and $p_{n,l}$ are sensitive to atomic structure and elemental composition of the topmost layers of the oxidized Cu(100) surface. The calculated $p_{n,l}$ with Cu 3s and 3p (O 1s) core electrons increase (decrease) with the decrease of the oxygen coverage. These results are consistent with the observed increase (decrease) of the intensity of the Cu M_{2,3}VV (O KLL) Auger signal as a result of annealing up to 300 °C, which causes O atoms to desorb or diffuse into the bulk. We interpret the decrease (increase) of the intensity of the Cu M_{2,3}VV (O KLL) Auger signal observed after the annealing temperature exceeds 300 °C as being due to diffusion of oxygen atoms from the bulk back to the surface where it would produce a re-
oxidation of the surface. Calculations confirm that the oxygen overlayer pushes the positron wave function from the top layer of Cu atoms away into the vacuum reducing (increasing) its overlap with Cu (O) atoms. Thus, re-oxidation leads to a large decrease (increase) in the positron annihilation probabilities with Cu 3s and 3p (O 1s) core electrons, and hence to a large decrease (increase) in the intensity of Cu M_{2,3}VV (O KLL) Auger signal in agreement with the experiment.

Calculations of positron surface states, positron work function and annihilation characteristics of the surface trapped positron with relevant core electrons were also performed for both Ga-rich and As-rich, ideally terminated, non-reconstructed GaAs(100) surfaces, and for the GaAs(100) surfaces with c(2×8), (2×4) and c(4×4) reconstructions. Theoretical positron binding energy, \( E_b \), positron work function, \( \Phi_p \), and positron annihilation probabilities with relevant core electrons, \( p_{n,l} \), computed for both As-rich and Ga-rich GaAs(100) surfaces are given in Tables 2 and 3, respectively.

### Table 2. Theoretical positron binding energy, \( E_b \), positron work function, \( \Phi_p \), and annihilation probabilities of the surface trapped positron with relevant core electrons, \( p_{n,l} \), computed for the As-rich GaAs(100) surface.

| Surface                  | \( E_b \) (eV) (theory) | \( \Phi_p \) (eV) (theory) | Annihilation probability (%) |
|--------------------------|-------------------------|-----------------------------|-----------------------------|
|                          |                         |                             | Core level                 |
|                          |                         |                             | As 3p                       |
|                          |                         |                             | As 3d                       |
|                          |                         |                             | Ga 3p                       |
|                          |                         |                             | Ga 3d                       |
| Nonreconstructed GaAs(100) | 2.63                    | -0.07                       | 0.50                        |
| Reconstructed GaAs(100)-c(2×8) | 2.54                    | -1.17                       | 0.43                        |
| Reconstructed GaAs(100)-(2×4) | 2.58                    | -0.95                       | 0.36                        |
| Reconstructed GaAs(100)-c(4×4) | 2.59                    | -0.68                       | 0.66                        |

It follows from the results presented in Tables that the computed values of \( E_b \) and \( \Phi_p \) are sensitive to the surface atomic structure and chemical composition of the top layers of the reconstructed GaAs(100) surface. Calculations confirm that localization and spatial extent of the positron surface-state wave function are both strongly affected by charge transfer, surface reconstructions and elemental content of the topmost layers of the GaAs(100) surface (see Figures 1 and 2). Theoretical \( p_{n,l} \) given in Tables 2 and 3 are also found to be sensitive to reconstruction and chemical composition of the topmost layers of the GaAs(100) surface.

### Table 3. Theoretical positron binding energy, \( E_b \), positron work function, \( \Phi_p \), and annihilation probability of surface trapped positrons with core level electrons, \( p_{n,l} \), computed for the Ga-rich GaAs(100) surface.

| Surface                  | \( E_b \) (eV) (theory) | \( \Phi_p \) (eV) (theory) | Annihilation probability (%) |
|--------------------------|-------------------------|-----------------------------|-----------------------------|
|                          |                         |                             | Core level                 |
|                          |                         |                             | As 3p                       |
|                          |                         |                             | As 3d                       |
|                          |                         |                             | Ga 3p                       |
|                          |                         |                             | Ga 3d                       |
| Nonreconstructed GaAs(100) | 1.76                    | -0.72                       | 0.06                        |
| Reconstructed GaAs(100)-c(2×8) | 1.77                    | -0.66                       | 0.37                        |
| Reconstructed GaAs(100)-(2×4) | 1.80                    | -0.17                       | 0.30                        |
| Reconstructed GaAs(100)-c(4×4) | 1.39                    | -0.74                       | 0.02                        |

It follows from Tables II and III that the experimental positron work function and annihilation probabilities of the surface trapped positron with As 3d, 3p, and Ga 3p core electrons agree best with theoretical \( \Phi_p \) and \( p_{n,l} \) computed for the Ga-rich reconstructed GaAs(100)-c(2×8) surface: -0.66 eV, 0.39%, 1.18%, and 0.15%.

### 4. Conclusions

The results of PAES studies of the oxidized Cu(100) single crystal and the GaAs(100) surface have been analyzed by performing calculations of positron surface and bulk states and positron annihilation...
characteristics taking into account the charge redistribution at the surface and surface reconstructions. Localization and spatial extent of the positron surface-state wave function, the positron binding energy, work function and annihilation characteristics of the surface trapped positron with relevant core-level electrons have been found to be sensitive to charge transfer, atomic structure and chemical composition of the topmost layers of the surfaces. Possible explanations have been proposed for the observed behavior of the intensity of positron annihilation induced Auger peaks measured from the oxidized Cu(100) single crystal and the GaAs(100) surface. The obtained results indicate that PAES could serve as an important surface diagnostic tool capable of distinguishing different oxide and semiconductor surfaces and defining their state of reconstruction.

**Figure 1.** Contour plot in the X-Z plane for Y = 0 of the positron surface state wave function at the As-rich reconstructed GaAs(100)-(2×4) surface. Contours are separated by 0.0012 atomic units.

**Figure 2.** Contour plot in the X-Z plane for Y = 0 of the positron surface state wave function at the Ga-rich reconstructed GaAs(100)-(2×4) surface. Contours are separated by 0.0014 atomic units.

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