AUGER SPECTRA OF SILICON DIOXIDE SURFACE DEFECT CENTERS

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**ABSTRACT**

It is shown that Auger electron spectroscopy can reveal the absolute energy level, with respect to the valence band edge, of Si dangling bond electrons in silicon dioxide. A theoretical model is proposed, and the Auger electron distribution N(E) for the LVV transition band is calculated for a stoichiometric silicon dioxide surface, and for a silicon oxide surface with unpaired, dangling bond electrons. The latter is characterized by an additional LVD transition band, where D is the energy level of the unpaired electron. The theoretical N(E) curves are compared with experimental N(E) curves for a pristine, and for...
20. Abstract (cont'd)

an electron radiation damaged quartz surface. Good agreement with the theoretical model is obtained, if D is assumed to lie 7.2 eV above the valence band edge.
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AUGER SPECTRA OF SiO₂ SURFACE DEFECT CENTERS

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ABSTRACT

It is shown that Auger electron spectroscopy (AES) can reveal the absolute energy level, with respect to the valence band edge, of Si dangling bond electrons in SiO₂. A theoretical model is proposed, and the Auger electron distribution NA(E) for the L₂₃VV transition band is calculated for a stoichiometric SiO₂ surface, and for a SiOₓ surface with unpaired, dangling bond electrons. The latter is characterized by an additional L₂₃VD transition band, where D is the energy level of the unpaired electron. The theoretical NA(E) curves are compared with experimental N(E) curves for a pristine, and for an electron radiation damaged quartz surface. Good agreement with the theoretical model is obtained, if D is assumed to lie 7.2 eV above the valence band edge.

INTRODUCTION

Further advances in military integrated circuit development require in-depth comprehension of many aspects of interface defects. Certain atomic-scale defects near the Si/SiO₂ interface unacceptably degrade the performance and reliability of MOS devices. This has become even more critical as IC devices move into the submicron regime. Improved techniques for identifying the chemical and electronic nature of these defects are a necessary prerequisite for eliminating them.

Radiation-induced intrinsic defect centers in SiO₂, or on its surfaces or interfaces, have been extensively studied by optical and electron spin resonance (ESR) techniques (for a review, see Refs. (1) and (2)). This paper proposes a theoretical model and presents preliminary experimental evidence on how these defect centers can be observed by AES.

The best known intrinsic defect is the E₁ (2), or E₅ center when it is a surface defect (3), which is an O⁻ vacancy and is characterized by an unpaired electron, strongly localized in a nonbounding sp³ orbital on a silicon bonded to just three oxygens. The unpaired electron or defect electron is less tightly bound to the Si atom than the other valence electrons, and its energy level in the energy-level scheme lies in the upper part of the band gap (2).

AES should be uniquely useful in revealing the absolute energy level of localized, occupied surface defect states. Because of the strong localization of the E₁ or E₅ center unpaired electron, this electron can be expected to participate in Auger transitions of the respective Si atom. Auger transitions involving valence electrons reflect the whole valence band. They do not just yield the energy difference between two levels of the proper separation without information on the absolute energy level of either, as most other spectroskopics do. Therefore, comparing a core-band-band Auger transition region with and without a defect state should reveal the absolute energy position of that defect state with respect to the valence band.
Fig. 1. Energy-level diagram showing a $L_{23}VV$ Auger transition at left, and three $L_{23}V_1V_1$ transitions.

**THEORETICAL MODEL**

For Si and SiO$_2$, the $L_{23}VV$ transition is the Auger process of highest probability. Such a solid-state Auger process is schematically shown in Fig. 1. The kinetic energy of the three Auger electrons resulting from the three $L_{23}VV$ Auger transitions indicated in Fig. 1 is always

$$E_A = 2E_V - E_{L_{23}} - E_{VAC}$$

The Auger electron distribution $N(E_A)$ is obtained by integrating over $\Delta$:

$$N(E_A) = \int_0^\infty W_A(E,\Delta) \cdot n(E+\Delta) \cdot n(E-\Delta) \cdot d\Delta$$

where $W_A(E,\Delta)$ is the matrix element for the Auger transition. The only complete one-body calculation (i.e., including matrix elements) of a core-valence-valence Auger line shape reported so far are those by Feibelman et al (4) for the $L_{23}VV$ transition band of a Si (111) surface. They find that in this case

$$W_A(E,\Delta) \cdot n(E+\Delta) \cdot n(E-\Delta) = n_p(E+\Delta) \cdot n_p(E-\Delta),$$

where $n_p(E)$ is the p-like component of the density of states (DOS). $N(E_A)$ is then a self-fold of $n_p(E)$. Assuming that the same relation also holds, at least approximately, for SiO$_2$ (and justifying this assumption from the agreement with experimental results), the Si K$\beta$ x-ray emission band from SiO$_2$ (5)
was chosen for \( n_p(E) \). \( n_p(E) \) is shown as the (local) density of states in Fig. 1. \( N(E_A) \) obtained from self-folding \( n_p(E) \) is shown in Fig. 2, together with an experimentally obtained \( N(E_A) \) for a pristine SiO\(_2\) surface. (Actually, it is \( N(E_A) \) superimposed on a background current of "true" secondary electrons.) The reasonably good agreement with the theoretical \( N(E_A) \) justifies the assumptions made in calculating \( N(E_A) \).

![Graph showing theoretical and experimental distributions](image)

**Fig. 2.** TOP: The theoretical \( L_{23VV} \) (full line) and \( L_{23VD} \) (dashed line) Auger transition bands. BOTTOM: Experimental secondary electron distribution \( N(E) \) from a pristine SiO\(_2\) surface (full line), and the difference between \( N(E) \) from an electron radiation damaged SiO\(_x\) surface, and \( N(E) \) from the pristine SiO\(_2\) surface.
If a defect level D due to an unpaired electron is included, an additional L\textsubscript{23}VD transition band is obtained. We assume that, at least in first approximation, n(E) for the defect-containing SiO\textsubscript{x} will be the same as for stoichiometric SiO\textsubscript{2}. This assumption is essential for our model, because it allows us to treat the L\textsubscript{23}VV spectrum of SiO\textsubscript{x} as a superposition of the L\textsubscript{23}VV band of stoichiometric SiO\textsubscript{2}, and the L\textsubscript{23}VD band. Conversely, it will allow us to experimentally obtain the L\textsubscript{23}VD band as the difference between the Auger spectra of SiO\textsubscript{x} and SiO\textsubscript{2}.

Figure 2 shows the L\textsubscript{23}VV and L\textsubscript{23}VD transition bands as separate components. D is assumed to be uniquely valued, and to lie 7.2 eV above the valence band edge, to make it consistent with the experimental results to be described later. We again consider only the p-like component of n(E). With the assumptions made, the shape of the L\textsubscript{23}VD transition band will be identical to the shape of np(E).

The experimentally collected Auger electron current distribution I\textsubscript{A}(E) is

\[ I\textsubscript{A}(E) \propto \int N\textsubscript{A}(E,x)e^{-x/d}dx \]

where x is the spatial coordinate perpendicular to the sample surface, x=0 describes the sample surface, and d is called "escape depth." For the SiO\textsubscript{2} L\textsubscript{23}VV transition considered here, the escape depth is only d \approx 4 Å (7). We should therefore expect to experimentally observe mostly surface defects.

**EXPERIMENTAL EXAMPLE**

Oxygen deficiency of SiO\textsubscript{2} surfaces can easily be created by electron irradiation. This effect has become known primarily as an annoyance in electron excited AES of SiO\textsubscript{2} surfaces (6). The observed decrease in the oxygen Auger signal is accompanied by changes in the L\textsubscript{23}VV Auger signal, the most pronounced of which is the appearance of a "Si peak" in the derivative mode (6,7).

Mitchell and Denure (8) have studied electron irradiation induced defect centers in SiO\textsubscript{2} thin films using cathodoluminescence spectra. They found that electron irradiation greatly enhances an optical emission peak ("C band") at \approx 4500 Å (2.8 eV), which the authors believe to be due to broken Si-O bonds (8). The growth law reported for this peak is the same as that reported for the AES "Si peak" (7), suggesting that both signals arise from the same defect center. Electron radiation damaged SiO\textsubscript{2} surfaces should therefore be a good example for testing our theoretical model.

The experimental Auger electron distribution curve shown in Fig. 2 was obtained from a quartz surface in the "as received" state by taking the Auger spectrum as fast as possible. (The spectrum was actually taken in the derivative mode, and integrated to obtain N(E).) The sample was then electron irradiated until the oxygen signal had decreased by 10%, and the Auger spectrum was taken again as fast as possible. The difference between the two N(E), which should correspond to the L\textsubscript{23}VD transition band, is shown as \Delta N(E) in Fig. 2. The peak P is a plasmon loss peak. Its energy and intensity are characteristic for a SiO\textsubscript{2} matrix. The maxima of \Delta N(E) and the theoretical L\textsubscript{23}VD transition band line up if D is assumed to lie 7.2 eV above the valence band edge, as shown in Fig. 1. This D level supplements the "C band" from cathodoluminescence (8) to exactly the SiO\textsubscript{2} band gap. We take
this as an indication of the validity of our model, and interpret the C band as arising from transitions from the bottom of the conduction band to the D level.

The principal ΔN(E) peak is somewhat broader than the theoretical peak. However, several simplifying assumptions were made in the model. One possible contribution to the broadening would be a finite width of the D level (assumed to be uniquely valued in the model) caused by a difference in the bonding strength for the unpaired electron between the outermost atomic layer and the next following atom layers.

A possible alternative interpretation for ΔN(E) would be Si islands in SiO₂ (6), because the absorption edges of the L₂3VD transition band and the Si L₂3VV transition band coincide approximately (and this information only is reflected in the maximum negative peak of the derivative mode spectrum). However, this should also be reflected in the plasmon loss spectrum, which we found to reflect strictly a SiO₂ matrix.

In summary, we find good agreement between the experimental example and the theoretical model, within the present limits of our general theoretical understanding of Auger transition line shapes.

REFERENCES


7. B. Carriè re and B. Lang, A study of the charging and dissociation of SiO₂ surfaces by AES, Surface Science 64, 209 (1977).