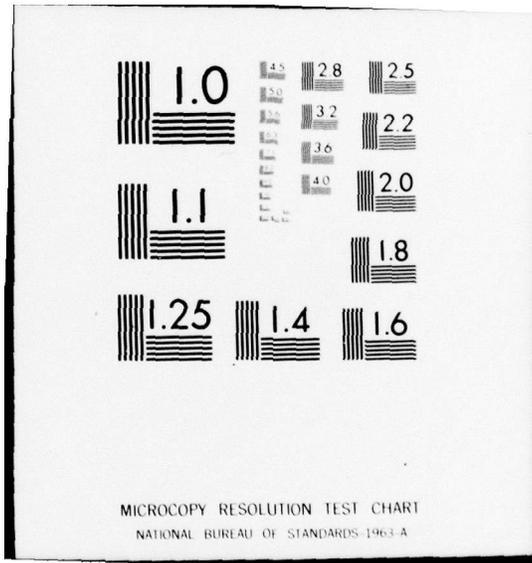


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**AUGER SPECTRA OF SILICON DIOXIDE SURFACE DEFECT CENTERS**

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JUL 19 1978  
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Klaus Schwidtal  
Electronics Technology & Devices Laboratory

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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 $\text{SiO}_2$ 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  $\text{SiO}_2$ . A theoretical model is proposed, and the Auger electron distribution  $N_A(E)$  for the  $L_{23}VV$  transition band is calculated for a stoichiometric  $\text{SiO}_2$  surface, and for a  $\text{SiO}_x$  surface with unpaired, dangling bond electrons. The latter is characterized by an additional  $L_{23}VD$  transition band, where D is the energy level of the unpaired electron. The theoretical  $N_A(E)$  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/ $\text{SiO}_2$  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  $\text{SiO}_2$ , 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  $E'_1$  (2). (or  $E'_s$  center when it is a surface defect (3)), which is an  $O^-$  vacancy and is characterized by an unpaired electron, strongly localized in a nonbonding  $sp^3$  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  $E'_1$  or  $E'_s$  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 spectroscopies 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.

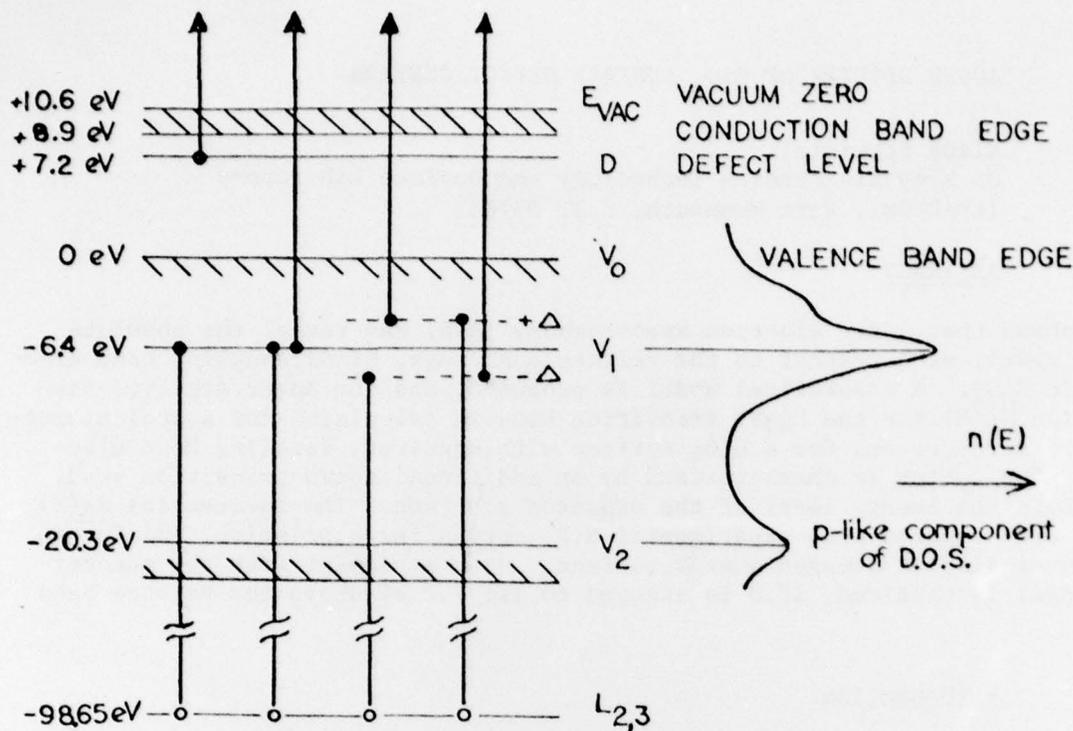


Fig. 1. Energy-level diagram showing a  $L_{23}VD$  Auger transition at left, and three  $L_{23}V_1V_1$  transitions.

#### 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

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

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

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

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  $\text{SiO}_2$  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  $N(E_A)$ .

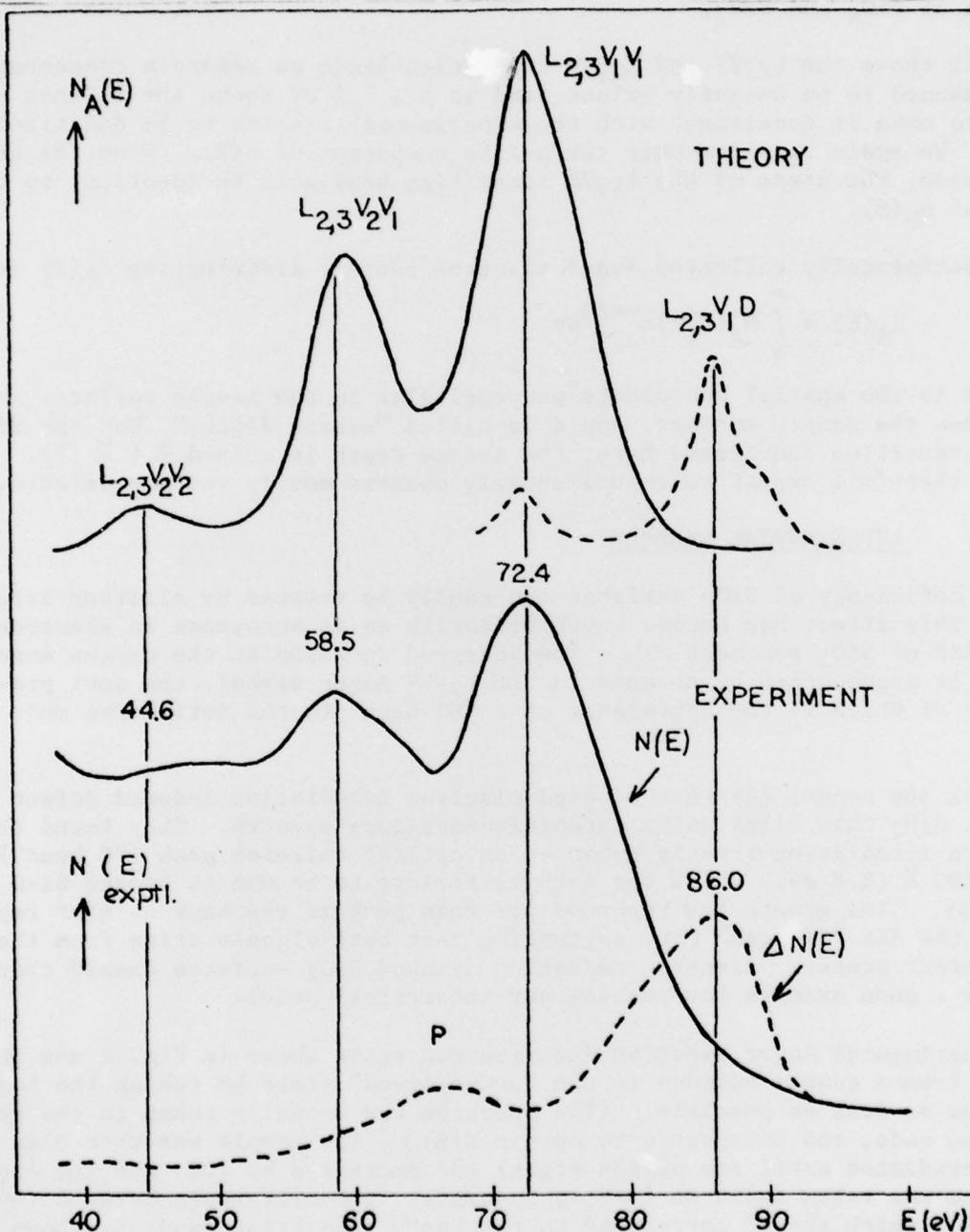


Fig. 2. TOP: The theoretical  $L_{23}VV$  (full line) and  $L_{23}VD$  (dashed line) Auger transition bands. BOTTOM: Experimental secondary electron distribution  $N(E)$  from a pristine  $\text{SiO}_2$  surface (full line), and the difference between  $N(E)$  from an electron radiation damaged  $\text{SiO}_x$  surface, and  $N(E)$  from the pristine  $\text{SiO}_2$  surface.

If a defect level D due to an unpaired electron is included, an additional  $L_{23}VD$  transition band is obtained. We assume that, at least in first approximation,  $n(E)$  for the defect-containing  $SiO_x$  will be the same as for stoichiometric  $SiO_2$ . This assumption is essential for our model, because it allows us to treat the  $L_{23}VV$  spectrum of  $SiO_x$  as a superposition of the  $L_{23}VV$  band of stoichiometric  $SiO_2$ , and the  $L_{23}VD$  band. Conversely, it will allow us to experimentally obtain the  $L_{23}VD$  band as the difference between the Auger spectra of  $SiO_x$  and  $SiO_2$ .

Figure 2 shows the  $L_{23}VV$  and  $L_{23}VD$  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  $L_{23}VD$  transition band will be identical to the shape of  $n_p(E)$ .

The experimentally collected Auger electron current distribution  $I_A(E)$  is

$$I_A(E) \propto \int_0^{\infty} N_A(E,x) e^{-x/d} dx$$

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  $SiO_2$   $L_{23}VV$  transition considered here, the escape depth is only  $d \approx 4 \text{ \AA}$  (7). We should therefore expect to experimentally observe mostly surface defects.

#### EXPERIMENTAL EXAMPLE

Oxygen deficiency of  $SiO_2$  surfaces can easily be created by electron irradiation. This effect has become known primarily as an annoyance in electron excited AES of  $SiO_2$  surfaces (6). The observed decrease in the oxygen Auger signal is accompanied by changes in the  $L_{23}VV$  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  $SiO_2$  thin films using cathodoluminescence spectra. They found that electron irradiation greatly enhances an optical emission peak ("C band") at  $\approx 4500 \text{ \AA}$  (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  $SiO_2$  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  $L_{23}VD$  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  $SiO_2$  matrix. The maxima of  $\Delta N(E)$  and the theoretical  $L_{23}VD$  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  $SiO_2$  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  $\Delta N(E)$  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  $\Delta N(E)$  would be Si islands in SiO<sub>2</sub> (6), because the absorption edges of the L<sub>23</sub>VD transition band and the Si L<sub>23</sub>VV 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 SiO<sub>2</sub> 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.

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