

## Tunneling Spectroscopy of Ultra-Thin Oxide on Si(111)

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Scanning tunneling microscopy (STM) methods are used in an air ambient to characterize 1.5 nm-thick SiO<sub>2</sub> on a degenerate Si structure. Two kinds of tunneling spectra are observed depending on measuring sites, here referred to as "normal" and "defect" sites. Spectra on the normal sites strongly depend on dopant types of substrates and reflect bulk band structures of Si together with SiO<sub>2</sub>/Si interface gap-states. Spectra on the defect sites show negative differential resistance (NDR) and the defect sites are identified on STM images as depressed areas. The origin of the NDR is ascribed to resonant tunneling through localized defects in the oxide.

### 1. INTRODUCTION

Scanning tunneling microscopy<sup>1)</sup> (STM) has been developed as a powerful technique to investigate metal and semiconductor surfaces. In particular, there have been many reports concerning Si on clean surfaces,<sup>2)-4)</sup> hydrogen-terminated surfaces<sup>5)</sup> and impurity adsorbed surfaces.<sup>6,7)</sup> However, SiO<sub>2</sub> on Si, which is most important in electronics applications, has been studied only in relation to digital current switching phenomenon.<sup>8)</sup> As was previously suggested,<sup>1)</sup> STM can be applied not only to conductive surfaces but also to insulating layers thin enough to permit electron tunneling. This paper presents, for the first time, tunneling spectroscopy of the ultra-thin oxide on degenerate p- and n-type Si obtained from STM measurements in an air ambient.

### 2. EXPERIMENTAL PROCEDURES

Degenerate Si with a dopant concentration of  $1 \times 10^{20} \text{ cm}^{-3}$  in the surface region was prepared to minimize band-bending effects with the help of B and As ion

implantation to p- and n-type Si(111) substrates, respectively. The background concentration of the substrates was  $5 \times 10^{18} \text{ cm}^{-3}$  for both dopant types. After successive annealing in N<sub>2</sub> at 900°C, the surface was oxidized in dry O<sub>2</sub> at 700°C. The resultant oxide thickness was determined to be about 1.5 nm by ellipsometry. The STM equipment used here is described in detail elsewhere.<sup>9)</sup> Electrochemically etched Pt-Ir probe tips were used. I-V spectra were acquired on more than five sites in an area of 50x50 nm<sup>2</sup> for each sample by momentarily opening the STM control feedback loop and sweeping tunneling voltage.

### 3. RESULTS AND DISCUSSION

Typical spectra for the 1.5 nm-thick SiO<sub>2</sub> on Si are shown in Fig.1 (a) for p- and (b) for n-type Si, where the dopant type dependence is obvious. Hereafter, this group of sites are referred to as "normal". It can be seen that the curvatures change with a tip bias voltage ( $V_{\text{tip}}$ ) of -1 V for p-type and  $V_{\text{tip}}$  of 1 V for n-type Si. The

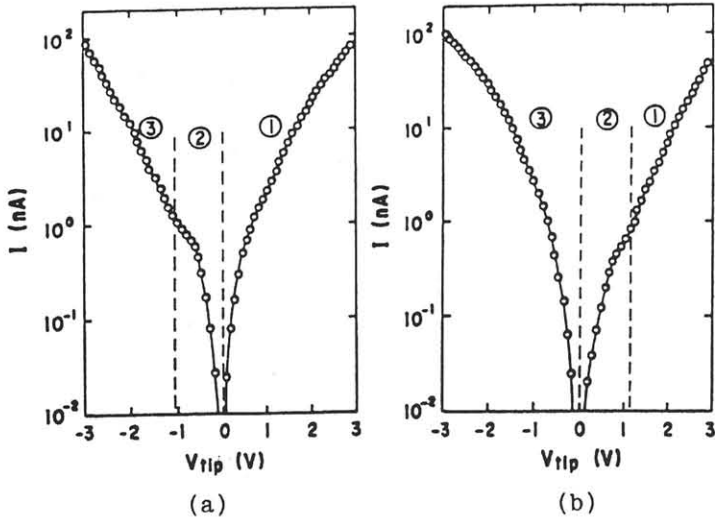


Fig. 1. Experimental I-V spectra on normal sites of 1.5-nm-thick  $\text{SiO}_2/\text{Si}$  samples. (a) and (b) are for p- and n-type substrates, respectively, with a surface concentration of about  $1 \times 10^{20} \text{ cm}^{-3}$ . Voltage regions designated by ①, ② and ③ correspond to different major current components as shown in Fig. 2.

voltages correspond to the band gap of Si substrates, as described below.

For analysis of the spectra, we calculated the direct band tunneling current for a simple planer metal-oxide-semiconductor (MOS) structure under a flat-band approximation, neglecting an air gap between the tip and the oxide surface. The calculation procedure followed a GaAs work by Feenstra et al.<sup>10)</sup> based on Harrison's formula.<sup>11)</sup> Figure 2 shows the calculated results for (a) p- and (b) n-type Si. The spectra can be divided into three bias regions corresponding to different current components of electrons as schematically illustrated in Fig. 2. Since the similarities between Figs. 1 and 2 are unequivocal, we conclude that the experiments can be qualitatively interpreted as direct tunneling reflecting Si band structure.

However, an appreciable difference between Figs. 1 (a) and 2 (a) is present in region ②. In Feenstra's work, although a similar difference was observed between the

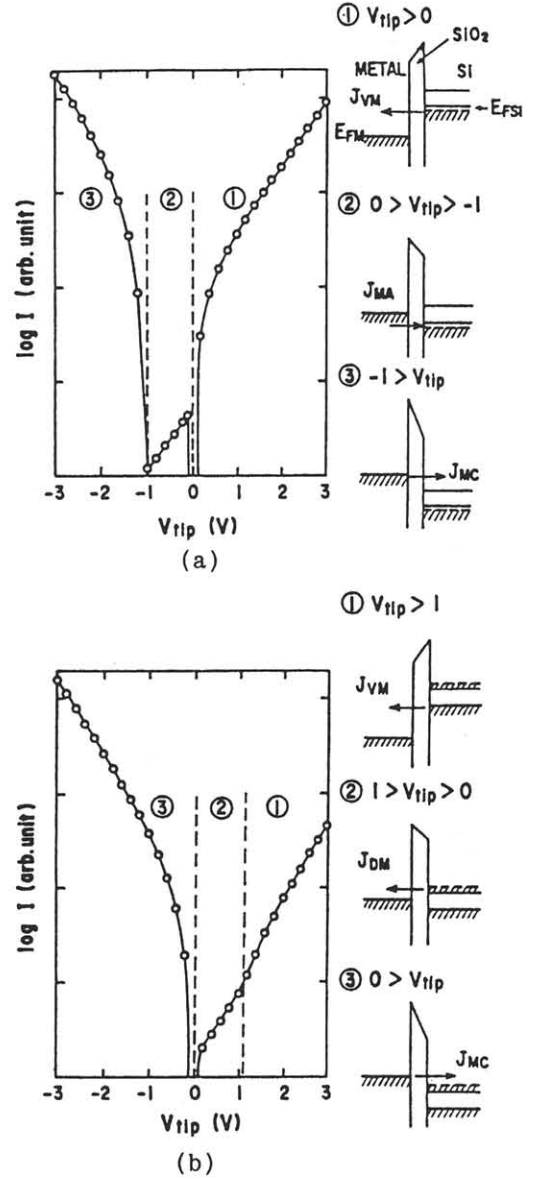


Fig. 2. Theoretical I-V spectra for (a) p-type and (b) n-type corresponding to Fig. 1. In this calculation, a planer MOS structure and the flat band condition are assumed. The major current component in each voltage region is also shown.  $J_{VM}$  denotes an electron flow from the valence band of Si to metal. Similarly,  $J_{MA}$  is from metal to the empty acceptor band,  $J_{MC}$  is from metal to the empty conduction band and  $J_{DM}$  is from the occupied donor band to metal.

flat-band calculation and the experiment for a p-type GaAs clean surface, more precise calculation, taking into account GaAs band bending, was found to be in good agreement with their experiment.<sup>10)</sup> However, this is not the case with the present experiment,

because band bending at zero bias is in the opposite direction. Therefore, in Fig.1 (a), we believe that an excess current component is added to the electron current from metal to the empty acceptor band,  $J_{MA}$ . This excess component can be ascribed to current flow through the oxide/Si interface gap-states, because electrons in metal near Fermi level readily flow into Si through the gap-states.<sup>12)</sup> Further study of this excess current might reveal the energy and spatial distribution of the gap-states.

In addition to the spectra of the normal sites, we observed another kind of spectra when changing measuring sites on the oxide. This group of sites are referred to as "defect". The I-V spectra on the defect sites are shown in Fig.3 (a) for p- and (b) for n-type Si. Negative differential resistance (NDR) is observed at about  $V_{tip}$  of 2 V in both spectra.

Figure 4 shows an STM image of the oxide on an n-type degenerate Si sample, where tunneling voltage and current were 0.5 V and 0.2 nA. The scanned area was  $50 \times 50 \text{ nm}^2$ . After acquiring the STM image, we measured I-V spectra on site A (protruded area) and site B (depressed area). As a result, we have found that A is a normal site showing a spectrum like Fig.1 (b), while B is a defect site showing a spectrum like Fig.3 (b). The same results were repeatedly obtained for different areas. Some ambiguity remains in this experiment because of thermal drift in the present experimental environment (1 nm or more per minute). However, the present result strongly suggests that the depressed areas are associated with the oxide defects, and thus each defect area has a typical size on the order of 10 nm.

Defects relevant to NDR should be inherent in the oxide, since, in our spectroscopy measurements of hydrogen-terminated Si, defect sites causing NDR had

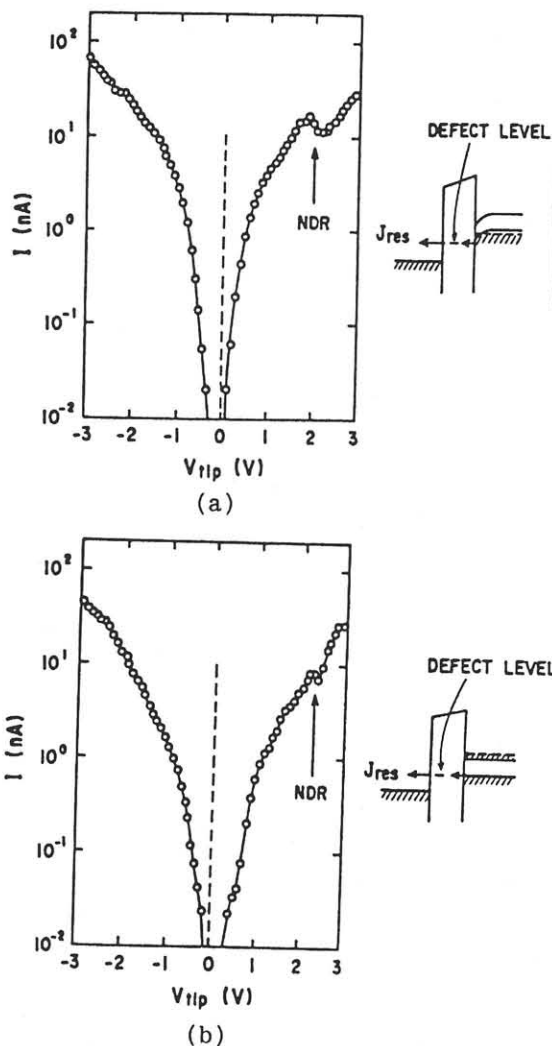


Fig.3. Experimental I-V spectra on defect sites of the same samples as in Fig.1. (a) and (b) are for p- and n-type substrates, respectively. Negative differential resistance (NDR) at a positive bias is indicated by an arrow. The resonant electron flow through the oxide defect,  $J_{res}$ , is also shown.

not been found and every spectrum belonged to the "normal" group.<sup>13)</sup> As an explanation relative to the oxide defects, we ascribe NDR to a resonant electron tunneling from the top of the Si valence band to the tip through the localized defect in the oxide. When the top of the Si valence band coincides with the defect level, the resonant current can flow in addition to the background of the direct tunneling current, as schematically shown by the insets in Fig.3. For higher bias

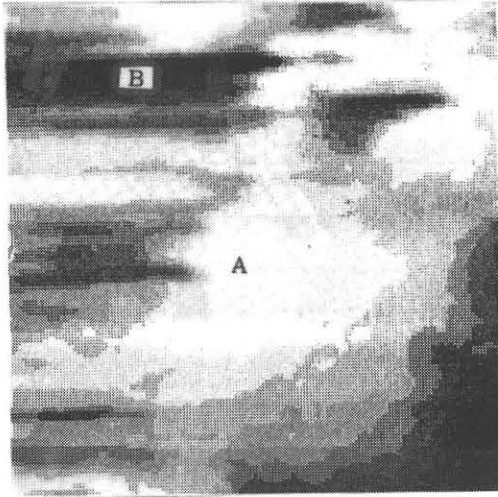


Fig.4. STM image of a 1.5-nm-thick  $\text{SiO}_2/\text{n-type Si}$  with an area of  $50 \times 50 \text{ nm}^2$  obtained at a tunneling voltage of 0.5 V and current of 0.2 nA. I-V spectra on site A (protruded site) and on site B (depressed site) are essentially the same as Fig.1 (b) and Fig.3 (b), respectively.

voltages (off-resonant conditions), the resonant current virtually disappears, since deeper valence electrons have less probability of tunneling.

It is not surprising that NDRs take place almost at the same voltages for both dopant types. This is because band bending for the p-type is as large as 0.7 V at  $V_{\text{tip}}$  of 2 V and mostly compensates the Fermi level difference of 1 V between p- and n-type Si. Therefore, an identical oxide defect with respect to energy level and depth from the surface can explain the experimental result for both dopant types.

#### 4. CONCLUSIONS

We have found with an STM in an air ambient that thin (1.5 nm) oxide on degenerate Si can be spatially categorized into two groups of sites, i.e., normal and defect. On normal sites, the I-V spectra are basically interpreted by the Si band structure and also by an additional current through oxide/Si gap-states. On defect sites, NDR was observed at about 2 V for both

dopant types. NDR is ascribed to a resonant current of valence electrons toward tip empty states through localized oxide defects. In STM images, the defect sites are strongly suggested to be located in depressed regions with an average size on the order of 10 nm. Thus, STM methods have been demonstrated to be applicable to insulating layers with microscopic spatial resolutions.

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