

## Interface States for Silicon Oxide Layers Formed by Use of Catalytic Activity of a Platinum Layer

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### 1. Introduction

Low temperature formation of gate oxide layers for MOS devices is one of the key techniques for the improvement of the device reliability and an increase in the number of components per IC chip. Metal-enhanced oxidation of Si is one of the candidates for the low temperature oxide formation. Although extensive studies have been performed using noble metals [1], transition metals [2], and alkali metals [3,4], the formation of sufficiently thick oxide layers applicable to gate oxide (i.e., more than ~5 nm) between the metals and the Si substrate has not been succeeded. We have recently developed a new method for the formation of sufficiently thick silicon oxide layers using a catalytic activity of a platinum (Pt) overlayer [5-7]. In this method, the interaction between the metal layer and the Si substrate is avoided by forming a ~1 nm-thick oxide layer before the metal deposition. Instead, a Pt layer which has a strong oxidation catalytic activity is employed in order to form active species (i.e., dissociated oxygen).

In the present study, the energy distribution of interface states for oxide layers formed by use of the Pt catalytic activity is investigated using a new method developed by us, i.e., XPS measurements under bias [8-10]. It is shown that the density of interface states can be decreased markedly by applying a bias voltage between the Pt layer and the Si substrate during the low temperature heat treatment.

### 2. Experiments

After chemically cleaning phosphorus-doped n-type Si(100) wafers with ~10 Ωcm resistivity, a ~1nm-thick oxide layer was formed by immersing the wafers in a concentrated nitric acid (HNO<sub>3</sub>) solution at 115 °C. Then, a ~4 nm-thick Pt layer was deposited by an electron beam evaporation method. The specimens with the <~4 nm-Pt/~1 nm-oxide/Si(100)> structure thus produced were heated at 300 °C in oxygen with a bias voltage applied between the Si substrate and the Pt layer.

XPS spectra were measured using a VG SCIENTIFIC ESCALAB 220i-XL spectrometer with a monochromatized Al Kα radiation source. For the determination of the energy distribution of interface states, the Pt layer was earthed and a bias voltage was applied to the rear Si surface during the XPS measurements [8-10].

### 3. Results and discussion

Figure 1 shows the XPS spectra in the Si 2p region for the <~4 nm-Pt/~1 nm-oxide/Si(100)> specimens after the heat treatment at 300 °C in oxygen for 2 h. A spectrum for the oxide layer formed in HNO<sub>3</sub> after the heat treatment at 300 °C is also shown [spectrum (a)] for comparison. From the ratio in the areal intensity of the oxide peak to that of the substrate peak, the oxide thickness was estimated to be 1.1 nm. This result shows that in the absence of the Pt catalytic layer,

the oxide thickness does not change by such a low temperature heat treatment. In the presence of the Pt layer, on the other hand, the oxide thickness greatly increased by the heat treatment at 300 °C. In this case, the application of a positive bias voltage to the Si with respect to the Pt layer greatly enhanced the oxidation [cf. spectra (b) and (c)] while a negative bias voltage retarded it [spectrum (d)]. When 3 V was applied to the Si, the thickness of the oxide layer increased to 7.9 nm after the 300 °C-heat treatment for 2 h. The presence of the oxide layer between the Pt overlayer and the Si substrate and its absence on the Pt layer were confirmed by cross-sectional transmission electron microscopy [5].

Figure 2 compares the energy distribution of interface states for the oxide layers formed by use of the Pt catalytic activity [spectra (a) and (b)] with that for the thermal oxide layer formed at 650 °C [spectrum (c)]. The interface state spectra were obtained from the analysis of the bias-induced shift of the substrate Si 2p peak measured as a function of the bias voltage [8-10]. It is seen that the oxide layers formed at low temperature using the Pt catalytic activity have lower interface state densities than the thermal oxide layer produced at higher temperature. For spectrum (a), no bias voltage was applied during the low temperature heat treatment, while 0.75 V was applied to the Si during the heat treatment. In both the spectra, a peak was present near the midgap, and it was attributed to isolated Si dangling bond states at the interface, on the basis of theoretical calculations using a density functional method [11]. The interface state density was decreased to ~1/4 by applying a positive bias voltage during the heating. The decrease in the interface state density is attributed to the formation of a smooth interface, as explained later.

Figure 3 shows the proposed mechanism for the Pt-enhanced oxidation. The enhancement of oxidation by applying a positive bias to the Si clearly shows that the moving species through the growing oxide layer is oxygen ions (O<sup>-</sup> and/or O<sup>2-</sup>). Initially, oxygen molecules are dissociated at the Pt surface [12], and the dissociated oxygen diffuses to the Pt/oxide interface. Then, oxygen ions are injected into the oxide layer. Oxygen ions migrate to the oxide/Si interface with the assistance of electric field in the oxide layer, and the reaction occurs there. Due to the enhancement of the migration of oxygen ions by electric field and to a small activation energy for the reaction of Si with dissociated oxygen ions, oxidation of Si easily occurs at low temperatures.

In the presence of nonuniformity of the oxide thickness, electric field in the thin region becomes higher than that in the thick region because it is in inverse proportion to the oxide thickness. Therefore, the migration rate of oxygen ions in the thin region becomes higher than that in the thick region, increasing the oxidation rate there. Consequently, the oxide thickness becomes more uniform and the inter-

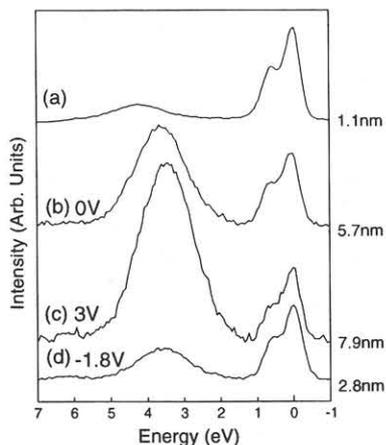


Fig. 1 XPS spectra in the Si 2p region observed after the heat treatment at 300 °C for 2 h in oxygen: (a) for the chemical oxide layer formed in  $\text{HNO}_3$ ; (b) for the  $\sim 4$  nm-Pt/silicon oxide/Si(100) specimen with no bias voltage applied during the heat treatment; (c) for the same specimen as (b) with 3 V applied to the Si with respect to the Pt during the heat treatment; (d) for the same specimen as (b) with -1.8 V bias during the heat treatment.

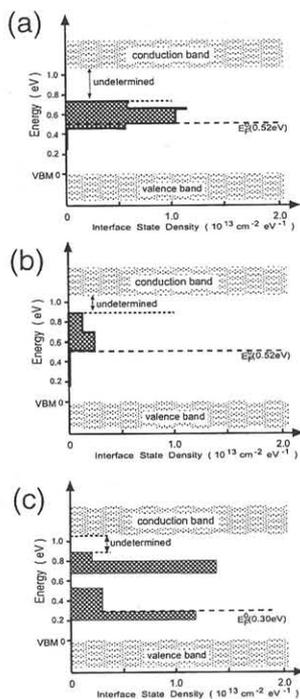


Fig. 2 Energy distribution of interface states for the  $\sim 4$  nm-Pt/silicon oxide/Si(100) specimen with the oxide layer formed by use of the Pt catalytic activity. For spectrum (a), no bias voltage was applied between the Pt and the Si during the heat treatment, while for spectrum (b), 0.75 V was applied to the Si with respect to the Pt. The interface state spectrum for the thermal oxide layer formed at 650 °C is also included for comparison [spectrum (c)].

face smoother. We have observed that the interface state density is greatly decreased by the formation of smooth interfaces [13]. Therefore, the decrease in the interface state density by applying the positive bias during the Pt-enhanced oxidation at the low temperature is attributed to the formation of a smooth interface.

#### 4. Conclusions

We have succeeded in the formation of the  $\sim 8$  nm-thick silicon

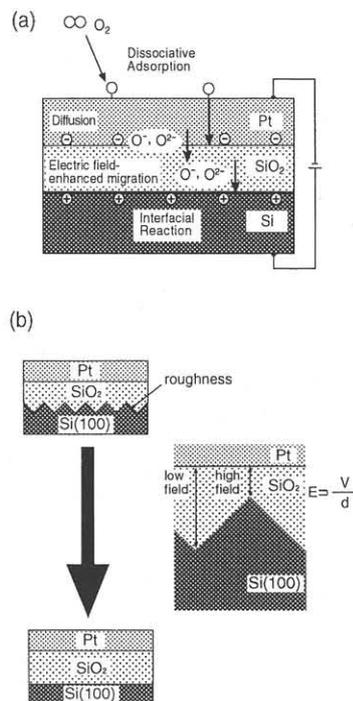


Fig. 3 Mechanism of the Pt-enhanced oxidation (a) and that of the formation of a smooth interface by applying a positive bias voltage to the Si with respect to the Pt during the heat treatment (b).

oxide layers at 300 °C by the oxidation of Si using the catalytic activity of the Pt layer. The oxidation is enhanced by applying a positive bias voltage to the Si with respect to the Pt layer during the heat treatment, showing that the moving species in the oxide layer is oxygen ions. The interface state density is greatly decreased by the application of the positive bias voltage to the Si during the oxidation, and it is attributed to the formation of a smooth interface.

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