Journal of Electron Spectroscopy and Related Phenomena 189 (2013) 56–60

Contents lists available at ScienceDirect

Journal of Electron Spectroscopy and Related Phenomena

journal homepage: www.elsevier.com/locate/elspec

Adsorption and reaction of titanium on an oxidized Si(0 0 1) surface

S. Ohno [a,*], S. Abe [a], K. Takahashi [b], M. Kamada [b], M. Tanaka [a]

[a] Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan
[b] Synchrotron Light Application Center, Saga University, Honjo 1, Saga 840-8502, Japan

ARTICLE INFO

Article history:
Received 11 April 2013
Received in revised form 12 June 2013
Accepted 16 June 2013
Available online 25 June 2013

Keywords:
Si surface
Oxidation
Photoelectron spectroscopy
Refractory metal

ABSTRACT

The adsorption and reaction of titanium on an oxidized Si(0 0 1) surface have been investigated using Si 2p, Ti 2p and O 1s core level photoemission measurements at room temperature (RT). We found that titanium adsorption on an oxidized Si(0 0 1) surface at RT causes a reduction of the intensity of the Si^{1+} and Si^{2+} states and an increase of the intensity of the Si^{3+} and Si^{4+} states. Based on an analysis of the Ti 2p and O 1s states, we conclude that the change in the Si 2p oxidized state upon titanium adsorption is due to charge transfer rather than conformation change.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The growth of titanium silicide ($TiSi_2$) and titanium oxide (TiO_2) on Si substrates has been intensively studied, because of the importance of these materials in complementary metal-oxide semiconductor (CMOS) technology. Titanium silicide nanostructures can be utilized for local interconnects due to their low resistivity and high stability [1]. Titanium oxide is a promising material as a high-k dielectric [2] and also has many other applications, e.g. in solar cells [3], batteries [4], and catalysts [5].

In the previous work, we have shown that enhanced oxidation of the silicon substrate occurs at the interface of Ti/Si(0 0 1) upon oxygen exposure at room temperature (RT) [6]. The results indicate that titanium acts as an effective catalyst for oxidation. There are two main features of this metal-promoted oxidation: one is to form thick silicon oxide film and the other is that the stoichiometry of the silicon oxide film is close to SiO_2. Based on the results of the present work, we deduce that re-estimation might be needed for the oxide thickness. In order to understand the latter feature, we investigated the reverse process, that is, titanium deposition on oxidized Si(0 0 1) at RT in detail.

High-resolution photoemission spectroscopy has been used to study deposition of metals such as Fe [7–10] and Co [11,12] on oxidized Si substrates. However, little work has been done on titanium, and we found that the electronic states are very different from those in the case of Fe and Co. Our present results for titanium suggest that two possible processes may be involved: enhanced oxidation or charge transfer. Here, we show that the latter is more plausible than the former.

2. Experimental

Photoelectron spectroscopy was carried out at the Saga University beamline BL13 in the Saga Light Source [13]. The photoelectrons for the Si 2p state were detected at normal emission ($\theta_e = 0^\circ$) or at the takeoff angle $\theta_e = 60^\circ$ with synchrotron X-rays at $h\nu = 130$ eV and 650 eV. The photoelectrons for the Ti 2p and O 1s states were detected at normal emission ($\theta_e = 0^\circ$) with synchrotron X-rays at $h\nu = 650$ eV. Binding energy was calibrated with the Au $4f_{5/2}$ and Au $4f_{7/2}$ photoemission peaks for each sample. The sample used was a n-type Si(0 0 1) single crystal with a resistivity of 1.0–10.0 Ω cm. Clean Si(0 0 1) was oxidized at an oxygen pressure of 1.0×10^{-5} Pa for 30 min (135 L) at RT. The thickness of titanium deposited on the oxidized Si(0 0 1) at RT was 0.3 nm (#1) or 0.45 nm (#2), as determined with a quartz microbalance.

3. Results and discussion

3.1. Analysis of the Si 2p state

Fig. 1 shows a series of Si 2p spectra. The surface component at −0.5 eV [14] diminishes while the Si 2p oxidized states (Si^{1+}, Si^{2+}, Si^{3+}, Si^{4+}) appear after oxygen exposure of 135 L at RT. The energy positions of the Si 2p oxidized states used for fitting are close to the values in Ref. [15]. Thickness of the silicon oxide film before titanium deposition was estimated to be 0.17 nm according to the

* Corresponding author. Tel.: +81 45 339 4200; fax +81 45 339 4200.
E-mail address: sohno@ynu.ac.jp (S. Ohno).

0368-2048/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.elspec.2013.06.009

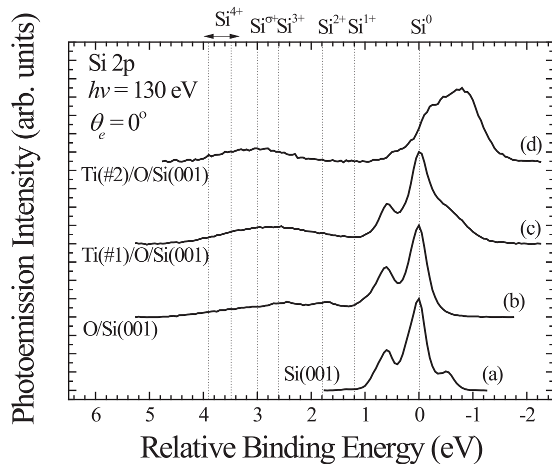

Fig. 1. A series of Si 2p spectra measured at the photon energy of 130 eV at RT for (a) a clean Si(0 0 1) surface, (b) an oxidized Si(0 0 1) surface after oxygen exposure of 135 L (1.0×10^{-5} Pa × 30 min) at RT, (c) a titanium-deposited surface at the thickness of 0.3 nm on oxidized Si(0 0 1) (#1), (d) a titanium-deposited surface at the thickness of 0.45 nm on oxidized Si(0 0 1) (#2).

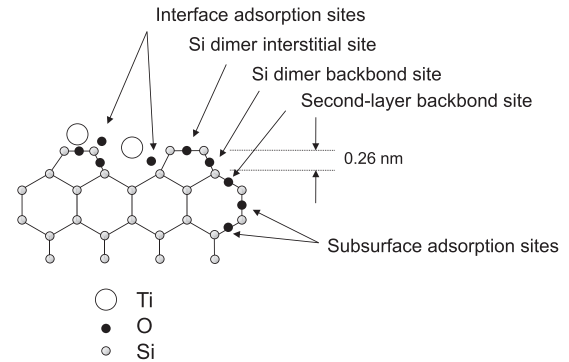

Fig. 2. Schematic of typical adsorption sites for oxygen and titanium in the titanium silicate ($SiTi_xO_y$) phase on Si(0 0 1).

conventional method [16]. It is known that oxygen can be adsorbed up to the backbond site at the present pressure regime [17,18]. The thickness of monolayer silicon oxide is considered to be ~0.3 nm, as shown in Fig. 2. The estimated value of 0.17 nm should be considered as the thickness on average. In other words, the surface may not be fully oxidized.

An additional component appears to be needed for fitting at the energy between the Si^{3+} and Si^{4+} states. We tentatively call this component the $Si^{\sigma+}$ state, and it is seen at 3.0 eV relative to the binding energy of the bulk Si^0 state. The results of the fitting are depicted in Fig. 3. The abundance ratio of the Si 2p oxidized states is summarized in Fig. 4. The ratio of the Si^{1+} state decreases rapidly upon titanium deposition at the thickness of 0.3 nm at RT. The Si^{1+} and Si^{2+} states both disappear at the thickness of 0.45 nm. In contrast, the ratio of the $Si^{\sigma+}$ state increases upon titanium deposition and reaches over 60% at the thickness of 0.45 nm. We present the intensity ratio of the sum of I(Si^{3+}) and half of I($Si^{\sigma+}$), and the sum of I(Si^{4+}) and half of I($Si^{\sigma+}$) in Fig. 4. The results indicate that the highly oxidized states (Si^{3+}, Si^{4+} and $Si^{\sigma+}$) are exclusively formed and no Si^{1+} and Si^{2+} remain at the thickness of 0.45 nm. It should be noted that the choice of the fitting parameters (peak position and FWHM) is important for the analysis of the Si 2p oxidized

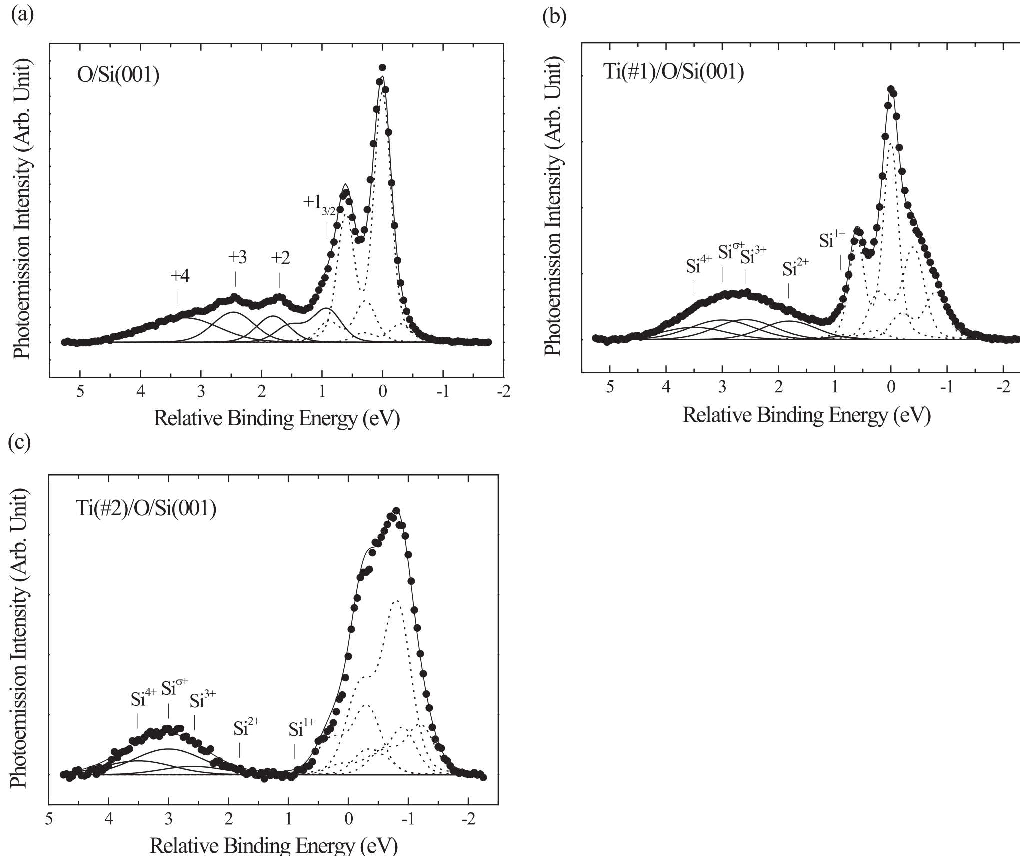

Fig. 3. Results of fitting for (a) an oxidized Si(0 0 1) surface after oxygen exposure of 135 L (1.0×10^{-5} Pa × 30 min) at RT, (b) a titanium-deposited surface at the thickness of 0.3 nm on oxidized Si(0 0 1) (#1), (c) a titanium-deposited surface at the thickness of 0.45 nm on oxidized Si(0 0 1) (#2).

Download English Version:

https://daneshyari.com/en/article/5396101

Download Persian Version:

https://daneshyari.com/article/5396101

Daneshyari.com