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X-ray photoelectron spectroscopy characterization of oxidated Si particles formed by pulsed ion-beam ablation

X.P. Zhu [a,*], Tomiyuki Yukawa [a], Makoto Hirai [a], Hisayuki Suematsu [a], Weihua Jiang [a], Kiyoshi Yatsui [a], H. Nishiyama [b], Y. Inoue [b]

[a] *Extreme Energy-Density Research Institute, Nagaoka University of Technology, 1 603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan*
[b] *Analysis Center, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-2188, Japan*

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Abstract

X-ray photoelectron spectroscopy (XPS) is used to probe oxidation states of Si species in particles deposited using a pulsed ion-beam evaporation method. The effects of He ambient gas, ion beam intensity and post-treatments on the oxides composition and oxygen content have been studied. It is found that presence of He ambient gas led to a profound oxidation of Si species as compared to that prepared in vacuum at the same ion-beam ablation energy, i.e. both increase of SiO_2 component and oxygen concentration in the oxides coverage. The deposition in He also resulted in an increase of oxygen concentration even under lower ablation intensity, but a higher Si suboxides concentration. It is revealed that the reaction between Si and O was controlled by the ion beam intensity (temperature of Si plasma) and the gas ambient (collision probability of Si and O species). The difference in structure of oxide layers for samples obtained under various conditions is discussed based on the results of XPS analyses.

Keywords: Silicon oxides; Pulsed ion-beam evaporation; Ablation plasma; X-ray photoelectron spectroscopy

1. Introduction

Si-based materials including Si oxides and crystalline Si are of great interests in many industrial applications such as in optoelectronics, microelectronics and biomedical areas, due to their unique electronic and optical properties [1–4]. A pulsed ion-beam deposition method, i.e. intense pulsed ion-beam evaporation (IBE), has been recently applied to study this category of materials, e.g. polycrystalline Si thin films and photoluminescent Si thin films/nanoparticles [5–7]. Among material syntheses by ablation plasma generated from a target material, this pulsed ion-beam approach is similar to pulsed laser deposition (PLD). Note that the pulsed ion-beam technique possesses several noticeable advantages over its laser

* Corresponding author. Tel.: +81 258 47 9891; fax: +81 258 47 9890.
E-mail address: xpzhu@nagaokaut.ac.jp (X.P. Zhu).

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counterpart, i.e. high efficiencies of beam generation and beam-target interaction, and large beam size that ensure high-rate, large-area deposition as well as surface modifications [8]. These characteristics are very attractive for practical applications. For instance, polycrystalline Si thin films and nanoparticles can be readily prepared in vacuum at room temperature [5–7] that is usually unavailable with PLD method and thus introduction of ambient gases, heating of substrates and/or high-temperature post-annealing were elaborated to improve the poor crystallinity of as-deposited Si species by PLD [9–11]. In our previous study, it was found that Si oxides played a major role in photoluminescence properties of IBE-prepared Si samples and the PL has been ascribed to defect bands in the Si oxide layers [7]. However, detailed dynamics of Si deposition by IBE is still not clear. In this paper, we present the study of oxidation phenomena of Si samples produced by the IBE process, using X-ray photoelectron spectroscopy (XPS) to probe the oxidation state of Si in samples prepared under different conditions, i.e. deposition in a vacuum, He gas ambient or changing the ion-beam ablation energy, and post-treatments in air (aged) and oxidation in O_2 gas at an elevated temperature (post-oxidized), respectively. Oxides composition and oxygen concentration have been compared for the different samples and main factors influencing the oxidation process is subsequently discussed.

2. Experimental

The deposition of Si samples was carried out in an intense pulsed ion-beam apparatus, ETIGO-II. The experimental scheme has been described in details previously [7]. A pulsed ion beam (~70 ns, 70 or 40 J/cm^2) was used to ablate a sintered polycrystalline silicon target, and subsequently the ablated Si species were deposited onto a lightly p-doped (1 0 0) Si substrate (10 mm × 10 mm, washed in a HF solution). The deposition was accomplished by a single shot of ion-beam ablation in a vacuum at 2×10^{-2} Pa or with a He ambient gas at 532 Pa, respectively. Prior to each one-shot deposition, the target was mechanically polished with 220# SiC papers to obtain a fresh surface and then loaded into the deposition chamber immediately to minimize their natural oxidation in air. All the Si samples were located at a target–substrate distance (d_{TS}) of 60 mm and in the center position of ablation plasma, where a deposited layer thickness is typically in the range of 100–200 nm depended on the varied parameters.

Measurements of XPS were performed on a JEOL JPS-100SX equipment using an unmonochromatized Mg Kα ($h\nu$ = 1253.6 eV) X-ray source with a 0.8-μm Al foil filter. The X-ray source was run at 200 W (10 kV and 20 mA). The X-ray beam with a circular cross-section area (~1 cm^2) was irradiated onto sample surface at an incident angle of 22.5° with respect to the surface plane and the photoelectrons were detected at 90° take off angle. Photoelectrons were analyzed with a concentric hemispherical analyzer at a pass energy of 30 eV. Under these conditions, the full widths at half-maximum (FWHM) of the Si 2p peaks of clean Si and SiO_2 (quartz) reference samples were about 1.4 and 2.0 eV, respectively. Furthermore, Ar^+ sputtering (800 V, 19 mA, 10^{-2} Pa) was applied to etch the samples for obtaining compositional information from the underlayers. The charging effects on the spectra have been corrected according to Au $4f_{7/2}$ peak at 84.0 eV.

3. Results and discussion

All the XPS curves were deconvoluted using Lorentzian–Gaussian functions after Shirley background subtraction. The peak fitting parameters are summarized in Table 1. A fitting process was conducted and optimized as follows. It was assumed that the intermediate oxidation states consist of Si^{1+}, Si^{2+} and Si^{3+} [12], i.e. Si suboxides SiO_x ($0 < x < 2$) and the binding energy of Si^{4+} is fixed to that of SiO_2 reference sample (103.4 eV). The spin-orbit splitting

Table 1
Summary of XPS spectra fitting results for Si samples prepared by IBE

Components	Peak position (eV)	FWHM (eV)
Si	99.1 ± 0.1 (99.3 ± 0.05)[a]	1.38
Si_2O	100.1 ± 0.05	1.58
SiO	101.2 ± 0.05	1.60
Si_2O_3	102.35 ± 0.05	1.78
SiO_2	103.4	2.0

[a] Values of samples after Ar^+ sputtering.