Thin Solid Films 518 (2010) S2–S5

Contents lists available at ScienceDirect

Thin Solid Films

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

# Low-temperature formation of silicon dioxide films by oxygen cluster ion beam assisted deposition

Hiromichi Ryuto [*,1], Takashi Yakushiji, Xin Jin, Gikan H. Takaoka

*Photonics and Electronics Science and Engineering Center, Kyoto University, Nishikyo, Kyoto 615-8510, Japan*

ARTICLE INFO

Available online 19 March 2010

*Keywords:*
Cluster ion beam
Silicon dioxide
Low-temperature deposition

ABSTRACT

Silicon dioxide films were formed by the cluster ion beam assisted deposition method. An oxygen cluster ion beam was irradiated while a silicon monoxide vapor was deposited on a substrate at room temperature. The deposited films were oxidized to form silicon dioxide films when the beam current density of the oxygen cluster ion beam was larger than 500 nA/cm$^2$ and the acceleration voltage of the oxygen cluster ion beam was higher than 3 kV.



## 1. Introduction

Silicon dioxide film has been extensively used in the semiconductor industry. A silicon dioxide film is usually formed by the thermal oxidation method or chemical vapor deposition. However, these methods require relatively high substrate temperatures, and a difficulty arises in applying these methods to materials such as polymers that has a relatively lower heat-resisting property. These materials are recently attracting much interest as materials to be used in the production of various displays. Therefore, a method to form a silicon dioxide film at low temperature is required for further application.

Silicon dioxide films were formed by the oxygen cluster ion beam assisted deposition method. A cluster is an aggregate of two to thousands of molecules bound by intermolecular forces, and the cluster ion beam assisted deposition method is a technique to irradiate cluster ion beam on the surface of the substrate while performing vapor deposition. The technique uses characteristic properties of cluster ion beams such as high density energy deposition to form high quality films [1]. Moreover, an oxidation effect is expected if an oxygen cluster ion beam is used in this technique. In this work, an oxygen cluster ion beam was irradiated on silicon substrates while vapor of silicon monoxide was supplied from a crucible.

## 2. Experimental procedure

Silicon dioxide films were formed on silicon substrates by the cluster ion beam assisted deposition method. Fig. 1 shows a schematic view of the apparatus for the cluster ion beam assisted deposition. The apparatus consists of an evaporation source for silicon monoxide and a part that produces an oxygen cluster ion beam, both of which are placed in a vacuum chamber. A substrate is placed at the upper part of the vacuum chamber, whose temperature is controlled using a lamp heater placed upper part of the substrate. The temperature of the substrate is measured using a thermocouple. The maximum temperature that the substrate can be heated is approximately 500 °C.

A mixture of oxygen and helium gas was filled in the gas container placed at the part of the apparatus drawn on the bottom right of Fig. 1. The mixing ratio of helium to oxygen gas was approximately 3/7 in volume, and the total pressure was typically 0.45 MPa. The helium gas is used as a carrier gas to accelerate cluster growth [2]. The gas was ejected into the vacuum chamber through a Laval nozzle, which results in the formation of oxygen clusters [3]. The middle part of the jet was selected using a 'skimmer' to avoid the fragmentation of clusters caused by shock waves. The skimmer is made of nickel and has a spherical cone shape. The skimmer is also used as a collimator that divides the vacuum chamber into high-vacuum and low-vacuum parts. The part in the vacuum chamber for cluster formation is evacuated using a roots pump and the part for the vapor deposition is evacuated using a turbo molecular pump. The typical pressure at the deposition part was approximately $1\times10^{-3}$ Pa during the deposition process. The clusters were ionized by the electrons emitted from the loop of a tungsten filament. The typical acceleration voltage and current of the electrons were 200 V and 200–300 mA, respectively. The typical distribution of the number of $O_2$ molecules per cluster (cluster size) had a peak approximately at 120. The monomer and cluster ions whose size was less than 100 were eliminated by the retarding voltage method applying a retarding voltage of 9 V. The retarding voltage method is based on the phenomenon that the velocity of the clusters formed by the expanding nozzle flow is fairly uniform within 10%, and the initial kinetic energy in the present case is expected to be 0.09 eV/molecule [2]. Then, the oxygen cluster ions were accelerated by the acceleration voltage from 1.5 to 9 kV. The transverse divergence of the cluster ion beam was suppressed using an electrostatic lens, and the beam was transported to the sample on

* Corresponding author. Tel.: +81 75 383 2339; fax: +81 75 383 2343.
*E-mail address:* ryuto@kuee.kyoto-u.ac.jp (H. Ryuto).

[1] Formerly, H. Akiyoshi.

0040-6090/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2010.03.025

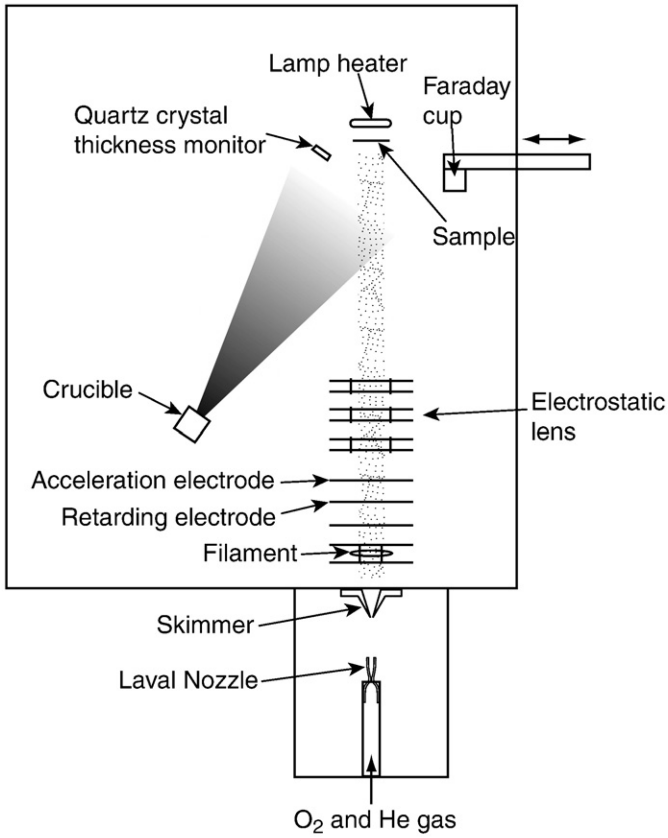


**Fig. 1.** Schematic view of cluster ion beam assisted deposition apparatus.

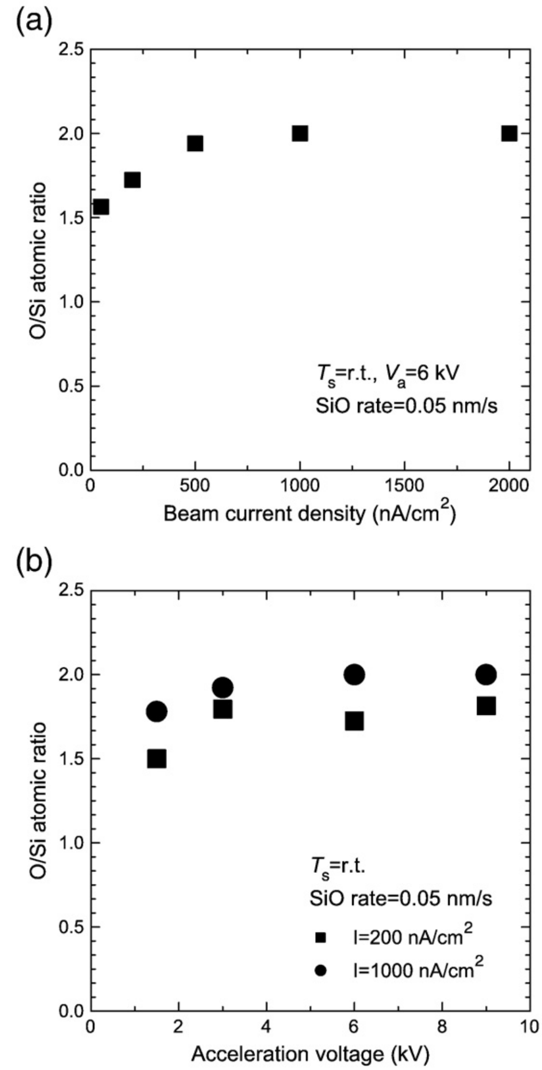


**Fig. 2.** Dependence of atomic ratio of oxygen to silicon of film on (a) beam current density and (b) acceleration voltage of oxygen cluster ion beam.

which the deposition was performed. A movable Faraday cup was inserted to the beam position and the intensity distribution of oxygen cluster ion beam was measured. The beam current density of the oxygen cluster ion beam was typically 2 μA/cm$^2$.

Grains of silicon monoxide were heated in a crucible using a tungsten heater, and vaporized for deposition. The purity of the silicon monoxide was 99.99%. The deposition was performed on approximately 15-mm-square n-type Si(100) substrates whose surface roughness was approximately 0.1 nm. The surface oxidation layer was removed by hydrofluoric acid. The deposition rate of silicon monoxide was measured continuously during the deposition using a quartz crystal microbalance film thickness monitor, and was controlled to keep a constant deposition rate by adjusting the heater power. The deposition rate was typically from 0.05 to 0.25 nm/s.

The atomic ratio between silicon and oxygen of the surface of the film deposited by the oxygen cluster ion beam assisted deposition was analyzed by X-ray photoelectron spectroscopy (XPS). The Fourier transform infrared (FTIR) spectroscopy analysis of the surface of the film was performed. The denseness of the film was analyzed by the etching rate in dilute hydrofluoric acid. The etching rate was measured by dipping the substrate masked using a Kapton tape into 1% hydrofluoric acid and measuring the depth using a step profiler.

## 3. Results and discussion

Fig. 2(a) shows a dependence of the atomic ratio of oxygen to silicon of the film formed by the oxygen cluster ion beam assisted deposition on the beam current density of oxygen cluster ion beam. The acceleration voltage of the oxygen cluster ion beam was 6 kV. The deposition rate of silicon monoxide was 0.05 nm/s. The substrate was at room temperature. The atomic ratio was approximately 1.5 when a neutral oxygen clusters were bombarded (without acceleration). The atomic ratio approached 2, which is the atomic ratio of silicon dioxide, with increase of beam current density of the oxygen cluster ion beam. Silicon dioxide films were formed when the beam current density was larger than approximately 500 nA/cm$^2$. So, considering the deposition rate of the silicon monoxide and the beam current density of the oxygen cluster ion beam, approximately one tenth of oxygen atoms in the cluster ion beam were used to form silicon dioxide.

Fig. 2(b) shows a dependence of atomic ratio of oxygen to silicon of the film on the acceleration voltage of the oxygen cluster ion beam. The deposition rate of silicon monoxide was 0.05 nm/s and the substrate was at room temperature. The beam current density of oxygen cluster ion beam was 200 nA/cm$^2$ or 1000 nA/cm$^2$. The ratios increased toward 2 with increasing acceleration voltage of oxygen cluster ion beams of beam current densities both of 200 and 1000 nA/cm$^2$, and were saturated when the acceleration voltage was higher than 3 kV. On the other hand, the atomic ratio of the film formed with a 1000 nA/cm$^2$ beam was higher than that formed with a 200 nA/cm$^2$ beam as were expected by the discussion of Fig. 2(a). The silicon monoxide layer is locally heated by the impact of an oxygen cluster ion during a short time [4], and the deposited energy to the silicon monoxide layer by an oxygen cluster ion is proportional to the acceleration voltage, so a higher acceleration voltage may enhance the oxidation. Therefore, the minimum acceleration voltage and beam