

# Nanocrystalline Si formation inside SiN<sub>x</sub> nanostructures using ionized N<sub>2</sub> gas bombardment

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Nanostructures of SiN<sub>x</sub> were made by bombardment of ionized N<sub>2</sub> on Si surface and subsequent annealing. Atomic force micrograph showed the density of SiN<sub>x</sub> nanostructures was  $3 \times 10^{10}/\text{cm}^2$ . Their lateral size and height were 40~60 nm and 15 nm, respectively. The chemical state of the nanostructure was measured using X-ray photoelectron spectroscopy, which changed from SiN<sub>x</sub> to Si<sub>3</sub>N<sub>4</sub> + SiN<sub>x</sub> as the bombarding ionized gas current increases. Upon annealing, transmission electron micrograph showed a clear evidence for crystalline Si phase formation inside the SiN<sub>x</sub> nanostructures. Photoluminescence peak observed at around 400 nm was thought to be originated from the interface states between the nanocrystalline Si and surrounding SiN<sub>x</sub> nanostructures

KEYWORDS : Si nanostructures, ion beam bombardment, XPS, SiN<sub>x</sub>, photoluminescence

## 1. Introduction

Recently, Si-based luminescent nanostructures such as nanocrystalline Si (nc-Si) have been investigated intensively for optoelectronic device applications [1-4]. In particular, many researchers have reported fabrication methods based on plasma-enhanced chemical vapor deposition (PECVD) and ion implantation [3] for the formation and control of Si-based nanostructures. A typical formation mechanism for the nc-Si is based on a self-organization process: transformation of non-stoichiometric SiN<sub>x</sub> or SiO<sub>x</sub> thin layers on a silicon substrate into ns-Si embedded in stoichiometric Si<sub>3</sub>N<sub>4</sub> or SiO<sub>2</sub> through the post-growth thermal annealing processes [1,5]. We have previously reported that SiN<sub>x</sub> nanostructures with average lateral size of 40 nm and the height of 5 nm could be formed

on a clean silicon surface by bombarding ionized N<sub>2</sub> gas and post-annealing [5]. Starting from SiO<sub>2</sub> covered Si substrate and using a similar method, we have also shown that SiO<sub>2</sub> nanostructures and bare Si surface were formed underneath SiN<sub>x</sub> capping layer. Thermal annealing produced nc-Si in the SiN<sub>x</sub> layer only on bare Si region [6].

In this paper, we report the formation of nc-Si inside SiN<sub>x</sub>. The initial SiN<sub>x</sub> nanostructure was formed by controlled bombardment of ionized N<sub>2</sub> gas. The nc-Si was then created by post-annealing the nanostructure as evidenced by transmission electron micrograph. The 400 nm photoluminescence peak observed was attributed to the interface states between the nanocrystalline Si and the SiN<sub>x</sub> capping layer.

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## II. Experimental Methods

We used commercially available (001) orientated silicon wafer for substrates, which were Sb-doped with a resistivity of 0.01  $\Omega\text{-cm}$ . The native oxide layer on Si was removed using RCA process in air before the wafers were put into the ultra-high vacuum (UHV) chamber (background pressure  $1 \times 10^{-10}$  Torr). The vacuum system was composed of an analysis chamber for the X-ray photoelectron spectroscopy (XPS) experiment, and an ion beam treatment chamber for the surface modifications. Samples were exposed to the ionized N<sub>2</sub> gas (N<sub>2</sub> 99.999 %) using a hot-filament ion gun at room temperature. To obtain various sample current densities, the gas pressure was changed from  $1.0 \times 10^{-8}$  to  $1.0 \times 10^{-6}$  Torr as well as the beam energy from 0.5 to 3 keV. The bombardment time was maintained at 30 min for all samples. Physico-chemically modified silicon surfaces were investigated by XPS and atomic force microscopy (AFM). The Si 2p, O 1s and N 1s core-level spectra and the binding energy 99.3 eV of Si 2p<sub>3/2</sub> for the clean silicon were obtained by referencing Au 4f<sub>7/2</sub> peak. The structural analysis was performed using high-resolution transmission electron microscopy (HR-TEM), and the luminescent properties of the nc-Si were determined using photoluminescence (PL) measurement.

## III. Results and Discussions

Figures 1(a) and 1(b) show Si 2p and N 1s XPS core-level spectra respectively with various ion current densities. As the sample current density increased, a broad peak clearly appeared at the binding energy range 100.0~102.0 eV in Si 2p core-level spectrum. The intensity of N 1s core-level similarly increased with increasing sample current density. Although not shown, there was no sign of O

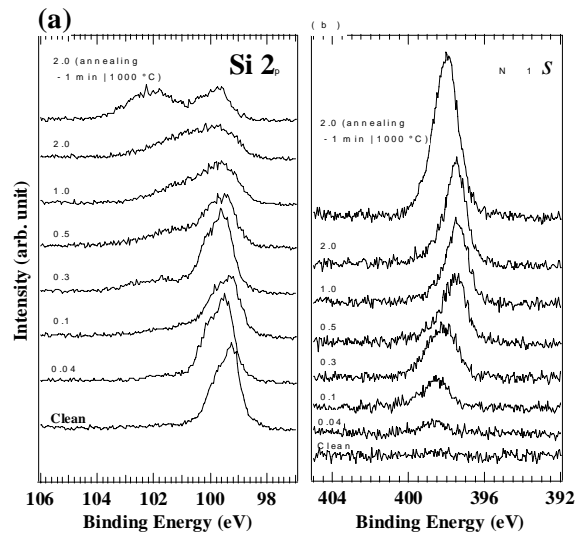


FIG. 1. (a) Si 2p and (b) N 1s core-level spectra with various N<sub>2</sub><sup>+</sup> ions current density ranging from 0.04 to 2.0 mA/cm<sup>2</sup>. The top spectrum is for the sample formed by the current density of 2.0 mA/cm<sup>2</sup> but annealed in N<sub>2</sub> gas environment of  $1.0 \times 10^{-8}$  Torr at 1000 °C for 1 min.

1s core-level peak, implying that oxygen impurity was not incorporated. The broad shape of the Si 2p peak was ascribed to the formation of SiN<sub>x</sub> with various x values [1,5]. After annealing this sample at 1000 °C for 1 min in N<sub>2</sub> gas of  $1.0 \times 10^{-8}$  Torr, the spectral intensity of Si 2p peak at ~102.0 eV significantly increased as seen in the top spectrum in Fig. 1(a). This means that chemical states on the surface were transformed to a more stable state such as Si<sub>3</sub>N<sub>4</sub> with the binding energy of 101.8 eV [1]. The peak intensity and width of N 1s core-level spectrum also increased after the annealing. It should be noted that the positions of N 1s peak for the samples with current density 0.04~0.3  $\mu\text{A}/\text{cm}^2$  were at the higher binding energy than those of other samples. This is the evidence that the chemical state of the samples with these ion current density ranges is that of SiN<sub>x</sub> by adsorption of nitrogen atom on Si [1]. For the samples with higher ion current density, we confirmed from Si 2p and N 1s core-level spectra that the chemical states are those of SiN<sub>x</sub> + Si<sub>3</sub>N<sub>4</sub>.

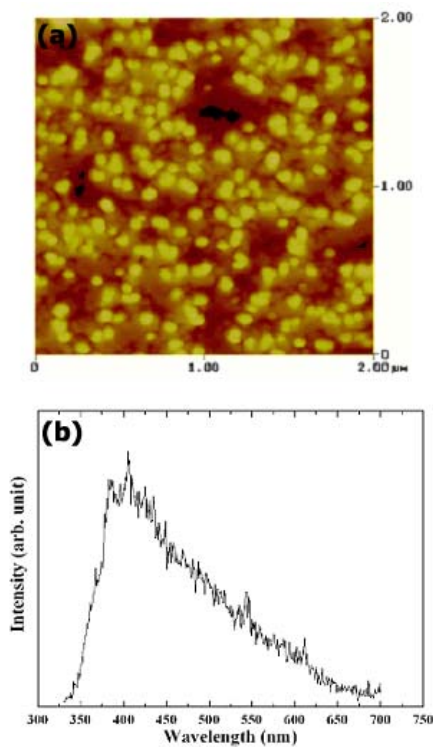


FIG. 2. (a) The AFM image for the annealed sample in Fig. 1. The lateral size and the height of nanostructures is 40~60 nm and 15 nm, respectively. (b) Room temperature PL spectrum for the annealed sample. Emission peak at around 400 nm is clearly visible.

Figures 2(a) and (b) show the AFM surface morphology and the room temperature photoluminescence (RT-PL) spectrum respectively for the sample formed using  $2.0 \text{ mA/cm}^2$  of  $\text{N}_2$  ion current density, and subsequently annealed at  $1000 \text{ }^\circ\text{C}$  for 1 min in  $1.0 \times 10^{-8}$  Torr of  $\text{N}_2$  gas environment. In the AFM image, randomly distributed nanostructures were observed on the surface. The lateral size and the height of nanostructures are 40~60 nm and 15 nm on average, respectively. The areal density of the nanostructures is  $3 \times 10^{10} / \text{cm}^2$ . It is noted that nanostructures formed by the ionized gas with the some kinetic energy are composed of  $\text{SiN}_x$  components and their shape is governed by the interactions at the interfaces. The differences in surface and interface energies between dissimilar materials such as  $\text{Si}_3\text{N}_4$ ,  $\text{SiN}_x$ , and nc-Si are thought to be origin of the

formation of observed nc-Si.

As shown in Fig. 2(b), RT-PL peak at the wavelength around 400 nm was obtained from the annealed sample. In order to confirm the origin of the luminescence, an HRTEM image of the cross-sectional view of the annealed sample was taken, as shown in Fig. 3. We found the nc-Si in  $\text{SiN}_x + \text{Si}_3\text{N}_4$  nanostructure. In the cross-sectional view, it is clearly seen that the nc-Si was located inside the nanostructures with the lateral size of 30 nm and the height of 10 nm. Although there is a possibility that the cross-sectional view offered an overlap of many nc-Si image with much smaller sizes, we could not draw definite conclusion. Therefore, we believe it is more reasonable to conclude that the observed PL spectra is due to the interface states that are formed between the nc-Si and  $\text{SiN}_x$  nanostructures or some defects in the Si structures and not due to the nc-Si clusters of sizes 3~4 nm. Finally, the mechanism of the creation of nc-Si in this work is firstly  $\text{SiN}_x$  nanostructures with the chemically metastable states are formed by the ionized  $\text{N}_2$  gas at room temperature; secondly nc-Si's are created in  $\text{SiN}_x$  nanostructures after annealing in ultra-high vacuum. During the annealing process, the chemically metastable states of  $\text{SiN}_x$  are transformed to the chemically stable  $\text{Si}_3\text{N}_4$ . The rest of Si atoms are transformed to nc-Si in the structural confinement around the chemical barrier of  $\text{Si}_3\text{N}_4$ .

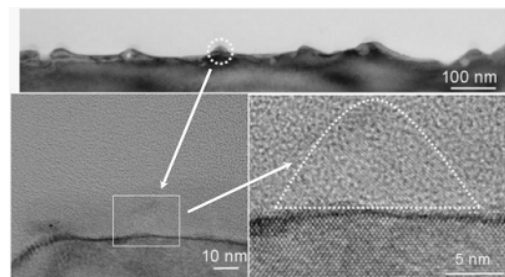


FIG. 3. The cross-sectional HRTEM images for the annealed sample. The crystalline phase of the Si is easily visible inside the nanostructures.

#### IV. Conclusions

The nc-Si's inside Si nitride nanostructures were formed by the ionized N<sub>2</sub> gas. The Si-nitride nanostructures have the chemical states of SiN<sub>x</sub> and Si<sub>3</sub>N<sub>4</sub> mixture above the ion current density of 0.5 mA/cm<sup>2</sup>. The nc-Si's with the lateral size of 30 nm and the height of 10 nm were located inside the nanostructures. We believe it is more reasonable to conclude that the observed PL spectra peaked at 400 nm is due to the interface states that are formed between the SiN<sub>x</sub> nanostructures and the nc-Si clusters of sizes much larger than 3~4 nm. The process described here offers an easy method for high density of nc-Si formation using ionized gas that is easily produced using commonly available ion guns.

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## 이온화 N<sub>2</sub> 가스 입사를 이용한 SiN<sub>x</sub> 나노구조 내부의 Si 나노결정 형성

정민철<sup>1</sup> · 박용주<sup>2</sup> · 신현준<sup>1</sup> · 변준석<sup>3</sup> · 윤재진<sup>3</sup> · 박용섭<sup>\*3</sup>

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실리콘 표면에 이온화된 N<sub>2</sub> 가스를 입사한 후 어닐링을 통해서 SiN<sub>x</sub> 나노구조를 형성하였다. 원자힘 현미경으로 관찰한 결과 이 나노구조의 밀도는  $3 \times 10^{10}/\text{cm}^2$  였으며, 가로 크기는 40~60 nm 이고 높이는 약 15 nm 임을 알 수 있었다. 엑스선 광전자 분광기술을 이용하여 이 나노구조의 화학상태를 측정하였는데, 입사하는 이온화된 N<sub>2</sub>의 단위시간당 양이 증가함에 따라서 화학상태가 SiN<sub>x</sub>에서 Si<sub>3</sub>N<sub>4</sub> + SiN<sub>x</sub> 형태로 변화함을 알 수 있었다. 열처리를 한 시료를 투과전자 현미경으로 측정된 결과는 SiN<sub>x</sub> 나노구조를 내부에 Si 나노 결정이 형성된 것을 보여주었다. 광여기 발광특성에서 관찰된 400 nm파장의 스펙트럼은 Si 나노결정의 크기를 고려할 때 나노결정과 SiN<sub>x</sub> 나노구조 사이의 계면상태에서 기인한 것으로 생각된다.

주제어 : Si 나노구조, 이온빔 입사, XPS, SiN<sub>x</sub>, PL

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