Oxygen (O)-terminated nanocrystalline silicon (nc-Si) films were prepared using silicon evaporation in an ultra-high vacuum with oxygen and argon radicals, and hydrogen (H)-termination of the nc-Si by HF solution treatment was tried in this work. The films were characterized by infrared (IR) absorption measurements in order to investigate the surface state of nc-Si in the films, which revealed that all of the Si-O bonds in the nc-Si films were replaced with Si-H bonds by HF solution treatment. The annealed samples exhibited strong photoluminescence (PL) with two peaks at ∼1.65 eV (∼750 nm) and ∼2.2 eV (∼560 nm), while no PL was observed from the H-terminated nc-Si. It was found that two PL signals are associated with Si-O related luminescence.

Keywords: Nanocrystalline silicon (nc-Si); HF solution treatment; Hydrogen (H)-termination; Infrared absorption spectroscopy; Photoluminescence

I. INTRODUCTION

Nanostuctures are of great interest and have been intensively investigated from the viewpoint of both fundamental physics and device applications, because they induce various quantum phenomena [1-6]. Nanocrystalline silicon (nc-Si) is expected as a visible light-emitting material for the application to optoelectronic integrated circuit (OEIC), where optical device are combined with present silicon-IC. It was reported that silicon crystals could exhibit a visible photoluminescence at room temperature when they were made very small [7]. In Ref. [7], a photoluminescence with a peak energy of 1.3 eV, which is much higher than the band gap for bulk silicon, was observed from ultra-fine (2-5 nm in diameter) silicon particle. Furthermore, it was reported that the wavelength of the luminescence became shorter with decreasing grain size [8]. In these report, silicon particles were produced by microwave plasma decomposition of SiH₄, H₂, and Ar gas mixture [8] or a planar magnetron RF sputtering technique in H₂ gas [7]. The silicon-evaporation technique is not mainly used for the preparation of silicon nano-particles. The advantage of this deposition method is the use of an elemental silicon source, which is safer and nontoxic, compared to SiH₄ gas. In this work, nc-Si films were prepared by silicon-evaporation in an ultra-high vacuum.

It is known that the nc-Si prepared by plasma CVD or RF sputtering was terminated with hydrogen atoms. On the other hand, the nc-Si films deposited in this study were terminated with oxygen atoms. Sato et al. reported that the PL intensity of HF-treated samples was higher than that of only annealed samples [9]. In this paper, H-termination of nc-Si films by HF solution treatment was carried out and the origin of the photoluminescence observed from the nc-Si films was discussed.

II. EXPERIMENTAL

The nc-Si:O films were deposited by silicon-evaporation in an ultra-high vacuum molecular beam epitaxy (MBE) chamber evacuated by a turbo-molecular pump. The base pressure of the MBE chamber was ∼5 × 10⁻⁷ Pa. (100)-oriented silicon was used as a substrate. High-purity silicon was evaporated by an electron-beam gun (3 kW) onto the substrate. The substrate was maintained at 500° throughout the growth. Oxygen and argon radicals were supplied during silicon-evaporation. The radical gun is equipped with an ion trap so that only neutral radicals are supplied to the substrate. The oxygen ratios in the source gases (O₂/(O₂+Ar)) were 20%. The chamber was maintained at a pressure of ∼10⁻⁴ Pa during the film deposition.

The deposited silicon films were annealed at 1000° for 1 hour in an Ar ambient. Subsequently the annealed samples were treated in HF solution (5%HF, RT, 1h). The structural properties were evaluated by infrared (IR) absorption measurements. The average grain size of nc-Si was estimated from the line width of X-ray diffraction (XRD) [10]. The photoluminescence (PL) spectra were measured at room temperature. An argon ion laser (488 nm, 2.5eV) with 50 mW was used as excitation sources. The PL signals were dispersed by a polychromator and detected by a cooled CCD detector.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the IR spectra for nc-Si films before and after the HF solution treatment. It is known that the
FIG. 1: IR spectra for nc-Si films before and after HF treatment. (a) 400-1400cm$^{-1}$ (b) Si-H$_x$ stretching mode region ($\sim$2100cm$^{-1}$).

FIG. 2: (a) IR spectra for nc-Si films with various film thicknesses after HF treatment at Si-H$_x$ stretching mode region. (b) IR spectra for nc-Si films with various film thicknesses after HF treatment and for Si substrate at Si-O-Si stretching mode region. (c) Relationship between film thicknesses and the amount of Si-H bonds in the nc-Si films.

bands at $\sim$580, $\sim$610 and $\sim$1100 cm$^{-1}$ correspond to Si-O rocking, Si-Si stretching and Si-O-Si stretching vibrations, respectively. The amount of Si-O$_x$ bonds were decreased after the HF treatment, while the absorption peaks which was originated from Si-H$_x$ bonds ($\sim$2100cm$^{-1}$) were observed as shown in Fig. 1(b).

Figures 2(a) and 2(b) show the IR spectra for nc-Si films after HF treatment with various film thicknesses at Si-H$_x$ stretching ($\sim$2100cm$^{-1}$) and at Si-O-Si stretching ($\sim$1100cm$^{-1}$) mode region, respectively. The normalized amount of Si-H bonds, which was estimated using the areas of the absorption peak around 2100cm$^{-1}$, is shown in Fig. 2(c). The amount of Si-H bonds was linearly increased with increasing the film thickness. As can be seen in Fig. 2(b), the amount of Si-O bonds was almost constant among the samples with various film thicknesses, and was the same level as the silicon substrate. It was found that the Si-O bonds observed after HF treatment was caused by the oxygen atoms originally existed in the substrate. These results indicate that all of the Si-O bonds in the nc-Si films were replaced with Si-H bonds by HF solution treatment.

Figure 3 shows the XRD spectra for the samples used in Fig. 1. The diffraction peak around $2\theta = 28.5^\circ$ corresponds to the Si(111) plane of c-Si. The average grain size of the nc-Si was estimated from the line width of the Si(111) diffraction peak. The average grain diameter before and after HF treatment was the same size (about 5 nm). It was revealed that oxygen atoms were substituted by hydrogen atoms at the surfaces of nc-Si by
means of HF solution treatment, with nc-Si remained.

Figure 4 shows the PL spectra for nc-Si films, (I) as-deposited sample, (II) annealed sample and (III) HF-treated sample. The broad PL bands at ~1.65 eV (~750 nm) and ~2.2 eV (~560 nm) were observed at room temperature. Two PL signals disappeared for the HF-treated sample, which indicates that two PL signals are associated with Si-O related luminescence.

Figure 5 shows the relationship between annealing temperature and the calculated grain size in the silicon films. It is confirmed that the average grain size of nc-Si increased with annealing temperature [11]. Nevertheless, the peak position at ~1.65 eV changes little with the annealing conditions, as shown in Fig. 6. The little dependence of the 1.65 eV peak position is incompatible with an explanation on the quantum size effect of nc-Si. These results indicate that the PL band at ~1.65 eV is related to the luminescence centers at the interface between nc-Si and silicon oxide matrix, which agrees with the three-region model proposed by Kanemitsu et al. [12].

Figure 7 shows the PL spectra for annealed samples in an Ar ambient at various annealing time. As shown in Fig. 7, the PL peak intensity at ~2.2 eV is monotonously weakened with increasing the annealing time. Additionally, the silicon oxide films on (100)-oriented Si, which was formed by thermal oxidation, also exhibited the PL band at ~2.2 eV. It is indicated that ~2.2 eV band originates from the defects related to oxygen.[13]

Photoluminescence caused by quantum size effects was not observed from both O-terminated and H-terminated nc-Si films in this work. Schuppler et al. reported that only silicon particles whose grain sizes were less than 1.5 nm contributed to visible PL emission [14]. It appeared
that the grain size of nc-Si prepared in this work was not small enough to exhibit quantum size effects.

**IV. CONCLUSIONS**

In this work, nc-Si:O films were deposited by silicon evaporation in an ultra-high vacuum. The deposited films were annealed at 1000°C in an Ar ambient. Subsequently, these samples were treated in HF solution in order to prepare the H-terminated nc-Si. The silicon films were characterized by IR absorption and XRD measurements. It was found that all of the Si-O bonds in the nc-Si films were replaced with Si-H bonds by HF solution treatment. The PL measurement was also carried out at room temperature. The strong PL was observed from the annealed samples at ∼1.65 eV and ∼2.2 eV, while no PL was observed from H-terminated nc-Si films. It was suggested that the ∼1.65 eV band originates in luminescence centers at the interface between nc-Si and silicon oxide matrix, while the ∼2.2 eV band results from the defects related to oxygen.