

Precise control over oxygen impurities in nano-crystalline silicon thin film processed with a low hydrogen dilution gas system at near room temperature



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ABSTRACT

An atmosphere highly diluted with hydrogen is essential to increase the crystal fraction during formation of hydrogenated nano-crystalline (nc) or micro-crystalline (μc) silicon thin films via chemical vapor deposition (CVD). This hydrogen-rich process, however, hinders the ability for the material to find adequate use in micro-electronic devices due to contamination that results in oxygen-related problems such as donor-like doping, defect creation, or passivation. The use of neutral beam assisted chemical vapor deposition (NBaCVD), with a low hydrogen ratio ($R = \text{H}_2/\text{SiH}_4$) of 4, successfully deposits a highly-crystallized nc-silicon (HC nc-Si) thin film (TF) at near room temperature ($<80^\circ\text{C}$) and effectively reduces oxygen contamination by as much as 100 times when compared to conventional plasma enhanced CVD. During the formation of HC nc-Si TF via NBaCVD, energetic hydrogen atoms directly react with oxygen atoms near the surface of the nc-Si TF and remove the oxygen impurities. This is a completely different mechanism from the hydrogen-enhanced oxygen diffusion model. This technology meets the recent requirements of a high deposition rate and low temperature necessary for flexible electronics.

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1. Introduction

It has been reported that a highly hydrogen-diluted PECVD process increases the crystal fraction in a micro-crystalline silicon ($\mu\text{c-Si}$) thin film. In order to produce a highly crystallized $\mu\text{c-Si}$ thin film via the conventional PECVD process, highly hydrogen-diluted silane gas systems should be used. Typically, the amount of the hydrogen dilution is measured through the use of the hydrogen ratio (R), which is defined as the effective gas flow ratio of hydrogen to silane (H_2/SiH_4). However, the PECVD process, with higher R ratios of up to 20 for a highly crystallized $\mu\text{c-Si}$ thin film, narrowly avoids disadvantages such as the reduction in deposition rate and increase in oxygen contamination. When depositing the thin film, hydrogen radicals enhance oxygen diffusion due to the decreasing activation energy of the oxygen diffusion path. Hydrogen-enhanced oxygen diffusion increases as the activation energy of the oxygen diffusion path decreases [1]. This oxygen impurity degrades the quality of $\mu\text{c-Si}$ thin film even when the thin film has a highly-crystallized large grain. In general, the high hydrogen ratio

increases both the crystal fraction and the oxygen content that tend to be located at the grain boundary. Sometimes, a higher oxygen content enhances crystallization and doping efficiency due to the greater defect density created by the oxygen [2,3]. However, oxygen-originated defects reduce mobility in most silicon-related thin films and devices [4,5]. In the matrix of micro- or nano-sized silicon crystals, oxygen impurities are located mostly at the grain boundary due to lattice stress and self-purification caused by the difference in the activation energy. The oxygen doped at the grain boundary increases the potential of the grain boundary [6,7]. These grain boundary states cause percolation [8] and hopping [9] characteristics to appear even in highly-crystallized Si thin films. Oxygen that is inhomogeneously distributed throughout the grain boundary leads to low conductivity, even when the thin film has a high crystal fraction, due to the antiparallel fluctuations of the band edges and band-gap-fluctuation-induced potential barriers [10]. A number of approaches have been investigated to reduce the occurrence of oxygen-related defects in the grain boundary while still obtaining highly-crystallized silicon, such as using a gas system with SiF_4 instead of one with SiH_4 [11], using getters in a gas purification process [12], and using a SiH_2Cl_2 precursor with CF_4 pre-cleaning [13].

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In this study, hydrogenated polymorphous (pm) Si thin films with evenly embedded nano-crystalline (nc) grains were deposited by using a brand new neutral beam assisted CVD (NBaCVD) system under various hydrogen ratio conditions at near room temperature (<80 °C). In traditional hydrogenated silicon deposition, the gas mixture ratio of hydrogen and silane (SiH_4) controls the phase of the thin films, including that from hydrogenated amorphous Si (a-Si:H) to $\mu\text{c-Si:H}$. Conversely, our deposition system, the NBaCVD system, directly controls the energy of the impinging hydrogen neutrals. This new technique micro-controls oxygen dopant concentrates in the nc-Si thin films and increases the crystal fraction under a low hydrogen ratio at near room temperature [14]. The NB source is comprised of a polished silicon wafer plate that acts as a conductor reflector, an internal ICP antenna that generates high-density plasma, and a termination capacitor (Cter, 50–1000 pF) [15] that is attached to the end of the ICP antenna and the ground to control the antenna surface potential as shown in Fig. 1. We set the optimized the Cter value in each experiment to minimize the peak-to-peak voltage of the antenna. This minimized antenna voltage is directly connected to the self-bias, owing to the surface potential distribution of the inductively coupled plasma (ICP) antenna. The newly developed NBaCVD technology controls the energy of neutral particles (mainly hydrogen atoms) in the range of 0–300 eV to enhance the crystallinity during thin film deposition at low temperatures [16–24].

2. Experiments

In this experimental system, process gases (Ar, Si, and H) are effectively ionized by the ICP antenna and are neutralized on the reflector surface. Hydrogen ions possess the highest probability of conversion by the polished silicon wafer reflector into a substantial neutral beam. The hydrogen neutral beam (H-NB) energies can be estimated to be about 87% of the impinging ion energies by using the simple binary collision model [25,26]. The hydrogen ions are accelerated in the plasma sheath between the plasma and the reflector, where the accelerating potential is the sum of the plasma potential and the biased voltage, and are then neutralized and recoiled primarily as a result of Auger neutralization [27]. The neutralization and recoil efficiency are dependent on the impinging angle, reflector material, surface roughness, etc. [28]. For instance, in the case of a bias voltage of -30 V and a plasma potential of 10 eV, the impinging H ions accelerate up to 40 eV, and the energy of the reflected H-NB particles then decreases to about 35 eV [16]. However, the effects of the Ar and Si neutral beams are negligible. Ar ions mainly work as sputtering species of the silicon reflector and have very poor reflection efficiency, as low as $\sim 3\%$, against the silicon solid because of the differences in mass. Meanwhile, silicon ions are deposited on, rather than reflected off, the silicon reflector surface. While deposition proceeds, the processing chamber with

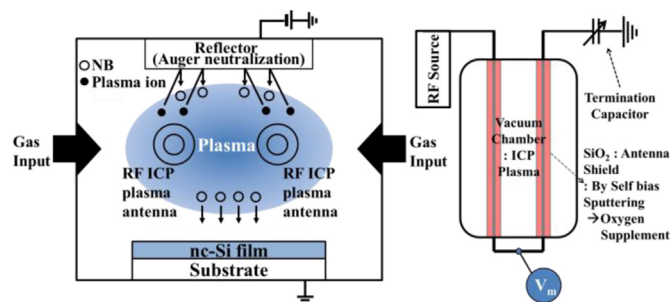


Fig. 1. Schematic diagram of the NBaCVD procedure and the neutral beam generation [14].

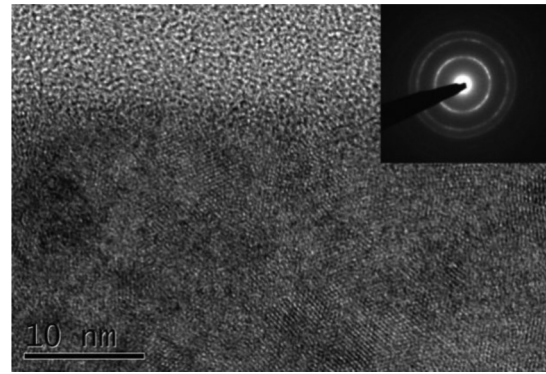


Fig. 2. nc-embedded pm-Si phases of nc-Si thin films deposited via the NBaCVD process with a low R ratio ($R = 4$).

the NB source is evacuated to a pressure of 1×10^{-6} Torr and operates at a working pressure of 2.2 mTorr. The processing gas mixture is comprised of SiH_4 , H_2 , He, and Ar. The RF power for the ICP antenna was fixed at 1100 W and the reflector biases for NB generation ranged from -40 to -240 V. All deposition processes were carried out at near room temperature. This NBaCVD process controls the energy of incident neutral particles (mainly H) in order to enhance the atomic activation and crystalline of thin films at near room temperatures (<80 °C). This NBaCVD process controls the energy of incident neutral particles (mainly H) in order to enhance the atomic activation and crystalline of thin films at near room temperatures (<80 °C). In traditional hydrogenated Si deposition via PECVD, the gas mixture ratio of H and Si controls the phase of thin films, such as a-Si:H, μc (or nc)-Si:H, while the substrate temperature determines the doping efficiency and crystal volume fraction, mainly. Conversely, the NBaCVD system can control the crystalline phase and the doping efficiency simultaneously by the energy of impinge neutral particles. During the deposition process, energetic H-neutral atoms transport their energy to the surface of depositing film to enhance crystallization (crystal volume fraction (X_c) $\sim 85\%$) and dopant activation ($\sim 1 \times 10^{20}$ #/cm³, ~ 30 cm²/V) with low H ratio at near room temperature on the substrate.

The structural state was estimated via Micro-Raman spectroscopy [633 nm, 15 mW, 1 μm spot diameter, Bomen (DA-8)], and the microstructure was analyzed via field emission transmission electron microscopy (FE-TEM, Tecnai G² F30 S-Twin). The concentration of oxygen impurities in the Si thin film was measured by using secondary ion mass spectroscopy (CAMECAIMS 7f magnetic sector SIMS). The silicon wafer substrate was used as reference for atomic concentration correction of each sample. The thickness of the thin films was measured using a long scan profiler (TencorP-2), and the thicknesses of SIMS-measured samples are kept at over 200 nm to avoid surface oxidation. The deposition rate is reduced from 4 Å/s down to 0.6 Å/s as the hydrogen ratio increases while an increase by no more than 10% is observed in case of a reflector bias increase.

3. Results and discussion

The TEM and Raman data suggest that the growth mechanism of the nc-Si thin film in the NBaCVD process differs from that of $\mu\text{c-Si}$ in the conventional PECVD process. The measured Raman spectra can be deconvoluted as several peaks as reported Lyou [29]. Generally in micro-crystalline Si thin-film, crystal peak move from 500 to 520 cm⁻¹ as increasing of crystal volume fraction. The reason of crystal peak's shift is grain size increases with crystal volume fraction. However, in the Raman spectra, crystal peak

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