Strong visible PL from the nc-Si thin film by Ni silicide mediated crystallization

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Abstract

We studied the growth of nanocrystalline silicon (nc-Si) thin film exhibiting a strong room temperature photoluminescence (PL) at 1.81–2.003 eV. The amorphous silicon was crystallized by Ni silicide mediated crystallization (Ni SMC) and then Secco-etched to exhibit the PL. The PL peak energy and intensity increase with increasing the metal density on the a-Si because of the reduction in the grain size down to 2 nm. The photoluminescence energy and peak intensity depend strongly on the Secco etch time because the grain size is reduced by etching the grain boundaries.

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PACS: 78.55.Ap; 78.66.Jg; 78.55.-m

Keywords: Nanocrystalline silicon; Photoluminescence

1. Introduction

After the first report of red photoluminescence (PL) in porous silicon [1], strong visible photoluminescence (PL) from nanocrystalline silicon (nc-Si) at room temperature has been extensively studied for the applications to Si-based optoelectronics [2–4]. Most of the previous studies have focused on the emission of visible light from the porous silicon.

In this work, we studied the novel growth technology of the nc-Si by Ni silicide mediated crystallization (SMC) to control luminescence energy [5]. Ni SMC was proposed to crystallize a-Si at low temperature for the low-temperature ply-Si (LTPS) on glass. A high-quality poly-Si was made by the thermal annealing at > 500°C of the a-Si film which was Ni plasma treated. The crystallization mechanism is understood as follows: The Ni atoms on the a-Si diffuse and form NiSi\textsubscript{2} precipitates, which grow gradually with time and finally become of critical size for crystallization. The crystallization starts from these precipitates until the collision with the other crystallites grown from the neighboring precipitates. Therefore, the grain size decreases with increasing the metal density on the a-Si [6].

We applied the SMC to make nanocrystalline silicon. The Secco etching, which is generally used for the etching of the grain boundary region of a poly-Si for SEM measurement, was used to control the grain size of the nanocrystallites.

2. Experimental

In this work, we have fabricated the nc-Si thin films by Ni SMC. First, a 1.4-\mu m a-Si:H film was deposited...
on glass by plasma-enhanced chemical vapor deposition (PECVD) at 250°C. The dehydrogenation was carried out by annealing the a-Si:H films on glass at 500°C. Second, Ni particles were scattered on the a-Si by sputtering of Ni rod with N₂. The deposited Ni density on the a-Si was 3.22×10¹⁵, 1.03×10¹⁶, and 1.22×10¹⁷ atoms/cm², respectively. The crystallization was carried out by annealing the a-Si films for 10 min at 600°C. Finally, the crystallized silicon films were treated by Secco etchant to reduce grain sizes of the nc-Si and remove the inter-grain amorphous region. Note that the grain boundaries are mostly composed of the amorphous phase.

3. Results and discussions

3.1. nc-Si film with different Ni density

Fig. 1 shows the PL spectra of the nc-Si thin films fabricated with different Ni densities. The nc-Si thin films made from the different Ni densities of 3.22×10¹⁵, 1.03×10¹⁶, and 1.22×10¹⁷ atoms/cm² on the a-Si exhibited the PL peak energies of 1.81, 1.84, and 2.003 eV, respectively. This means that the luminescence energy can be controlled by the Ni density on the a-Si.

Fig. 2 shows the full-width at half-maximum (FWHM) of the [220] XRD peaks and the intensity of the [111] XRD peaks of the nc-Si films crystallized with various Ni densities. As can be expected from the PL spectra, the FWHM of the [220] XRD peak increases with the increase of Ni density. The increase of the FWHM means the reduction of grain size. On the other hand, the intensity of the [111] XRD peak decreases with the increase of Ni density. The decrease of the [111] peak intensity means that [111] needle-like growth of the nc-Si grains is restrained. This indicates that the grain size of the nc-Si decreases with increasing the Ni density. Therefore, the red luminescence is due to the quantum confinement effect [7–9].

Fig. 3 shows the PL peak energy and PL peak intensity shown in Fig. 1 and optical band gap energy obtained from optical absorption measurement. Both PL peak energy and optical band gap shows a blue shift with an increase of Ni density. However, for the nc-Si thin film with the same Ni density, PL peak
energy and optical band gap show a great difference. The difference between the two energies expands with the increase of Ni density. The difference may be due to the self-trapped exciton state (STE) [10].

When the energy of self-trapped exciton is high enough, the room temperature PL can be seen. If it is smaller than 0.1 eV, the PL can be detected only at very low temperature. The difference in this work is 0.4–0.5 eV, which is enough to emit the room temperature PL as in the case of the polymer semiconductor exhibiting strong light emission at room temperature. The PL peak intensity increases with the Ni density on the a-Si. This increase is related to the increase in the transition probability for radiative recombination as a result of the reduction in the grain size of the nc-Si [11–14]

3.2. nc-Si film with various Secco etching times

Fig. 4 shows the PL spectra of the nc-Si thin films with various Secco etching times. The PL peaks at ∼450 and ∼830 nm decrease with increasing Secco etching time and finally disappear. However, PL peak at ∼680 nm appears by Secco etchant treatment and increase with increasing etching time. Note that the nc-Si film without Secco etchant treatment does not exhibit red PL. It appears to remove the defects and weak bonds at the grain boundary regions. The Secco etchant is used in the surface treatment of the poly-Si for SEM image. This is due to the different etching rates between grain (c-Si) and grain boundary (a-Si). After Secco etchant treatment, amorphous region of the nc-Si thin film is removed. In addition, Secco etchant treatment can passivate the dangling bonds in the grain boundaries of the nc-Si by hydrogen. Therefore, PL peaks at ∼680 nm appears after Secco etchant treatment and increase with Secco etching time.

However, the PL peaks at ∼450 and ∼830 nm disappear after Secco etching. This may be due to the HF in Secco etchant. It is known that the PL peaks at ∼450 and ∼830 nm are due to the SiO2 which can be etched by HF [15]. Therefore, the PL intensities decrease with increasing Secco etching time.
Fig. 5. The FWHM of XRD [220] intensity of the nc-Si thin films treated with various Secco etching times.

Fig. 6. The FWHM and Raman intensity of the nc-Si thin films at various Secco etching times.

Fig. 5 shows the [2 2 0] FWHM of XRD intensity as function of Secco etching time. The FWHM increases with increasing Secco etch time. The FWHM decreases generally with the increase of grain size. Therefore, the grain size decreases down to 2 nm with increasing the Secco etchant treatment. The grain size can be reduced as a result of etching the grain boundaries of the nc-Si.

Fig. 6 exhibits the FWHM and the peak position of the Raman shift as function of Secco etching time. The Raman shift decreases and the FWHM increases as the result of the reduction in the grain size.

4. Conclusion

We studied the novel fabrication technology of the nc-Si thin films using Ni SMC. Luminescence wavelength can be tuned by controlling Ni density on the a-Si. The nc-Si thin films by Ni SMC of a-Si exhibited strong PL at 1.81–2.003 eV at room temperature. On the other hand, the optical band gap of the nc-Si increases from 2.17 to 2.5 eV with increasing the Ni density on the a-Si. The difference between the PL peak energy and optical band gap energy is due to the self-trapped excitons. The high optical band gap and red PL of the nc-Si thin films are explained by quantum confinement effect.

References