Fabrication of nano-crystalline silicon thin film at low temperature by using a neutral beam deposition method

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ABSTRACT

Low temperature ($< 80\,°C$) neutral beam deposition (LTNBD) was investigated as a new approach to the fabrication and development of nano-crystalline silicon (nc-Si), which has better properties than that of amorphous silicon (α-Si). The difference between LTNBD and conventional PECVD is that the film formation energy of the nc-Si in LTNBD is supplied by controlled neutral beam energies at a low temperature rather than by heating. Especially, in this study, the characteristics of the nc-Si thin film were investigated by adding 10% of an inert gas such as Ne, Ar or Xe to SiH_4/H_2. Increasing the beam energy resulted in an increase in the deposition rate, but the crystallinity was decreased, due to the increased damage to the substrate. However, the addition of a higher mass inert gas to the gas mixture at a fixed beam energy resulted not only in a higher deposition rate but also in a higher crystallization volume fraction. The high resolution transmission electron microscopy image showed that the grown film is composed of about 10 nm-size grains.

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1. Introduction

Crystalline silicon (c-Si) thin films (nano-crystalline silicon: nc-Si, or microcrystalline silicon: μc-Si) are generally applied to electronic and optoelectronic devices, because of their higher carrier mobility than that of amorphous silicon (α-Si) films and excellent potential in fabricating higher speed and higher resolution thin film transistor–liquid crystal displays (TFT–LCDs) or active matrix organic light emitting diodes (AMOLEDs). In addition, c-Si thin films can provide higher electrical conductivity than α-Si and have a low possibility of the degradation of their electrical properties, resulting from the loss of hydrogen in the amorphous silicon. Currently, c-Si thin films are fabricated by crystallizing α-Si films deposited by plasma enhanced chemical vapor deposition (PECVD) with a post-treatment method such as excimer laser annealing (ELA), solid phase crystallization (SPC), metal-induced crystallization (MIC), etc. [1–4]. However, these troublesome post-treatments require a high processing temperature (500–600 °C), which is higher than the glass transition temperature. Furthermore, throughput and cost issues become more critical as the substrate size is increased.

If c-Si were able to be deposited on plastic substrates at a low temperature, it would reduce the fabrication cost significantly and this technique could be used for next generation displays such as flexible displays. Also, a technique that allows for c-Si TFTs to be fabricated on plastic substrates could be applied to the fabrication of other electronic devices such as smart card, new non-volatile memory, and portable electronics. Therefore, to simplify the process steps and increase the production throughput, the direct deposition of c-Si at a low temperature (usually nc-Si not μc-Si at a low temperature deposition) is definitely required.

nc-Si:H thin films can be directly deposited by conventional PECVD at a low temperature with very high H_2 percentages in the SiH_4/H_2 gas mixture, but it is known that the deposition rate must be kept extremely low to obtain a reasonable crystallization volume fraction. Therefore, for the direct deposition of nc-Si:H at a low temperature, alternative ideas have been proposed instead of the conventional PECVD method [5], such as ion beam irradiation or substrate biasing during the deposition of the silicon film in order to use the kinetic energy of the bombarding ions incident on the growing film surface for crystal growth [6–9]. Bae et al. [6] reported that the rf-substrate bias increases the

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crystallinity of the silicon deposited by the electron cyclotron resonance PECVD method. Swain et al. [7] also reported that the application of a negative bias increases the crystallite size and crystalline fraction of the nc-Si deposited by the hot-wire CVD. Nozawa et al. [8] studied the effect of substrate bias on crystallinity from the point of view of ion energy, ion flux, and substrate temperature. Saha et al. [9] deposited nc-Si directly at a low temperature by using an ion beam sputtering method and the nc-Si deposited by this technique was compared with that deposited by the plasma-based process.

In this study, as an alternate method of supplying the energy to the particles bombarding the substrate surface during the nc-Si:H deposition at a low temperature, low temperature neutral beam deposition (LTNBD) is investigated. LTNBD is performed by using a gas mixture of SiH_4/H_2 as a deposition source, that is the deposited films contain a significant fraction of hydrogen atoms. We used a neutral beam instead of an ion beam in the bombardment of the substrate surface, in order to prevent any possible charge-related damage to the growing nc-Si:H thin film. The effect of additive inert gases such as Ne, Ar, and Xe and in some cases, the effect of the energy of the bombarding particles on the characteristics of the grown nc-Si thin films were investigated.

2. Experimental details

Fig. 1 shows a schematic diagram of the neutral beam deposition system used for the fabrication of the nc-Si:H films. The neutral beam source was composed of a 15 cm-diameter inductively coupled plasma (ICP) ion gun with two grids for the acceleration of the reactive ions in addition to the formation of reactive radicals and a low angle parallel plate reflector made of graphite for the neutralization of the reactive ions. The energetic ion beam was extracted from the ICP ion gun by the grid system and the extracted ion beam was neutralized by reflecting on the parallel reflecting plates, which are tilted at an angle of 5° to the ion beam direction for the low angle reflection of the extracted ion beam. The details of the neutral beam deposition system used in the experiment can be found elsewhere [10].

To grow the nc-Si:H thin films, a gas mixture of SiH_4 (10 sccm)/ H_2 (80 sccm) was fed to the ICP ion gun source while applying an rf power of 500 W at 13.56 MHz to the ICP source. In addition, in
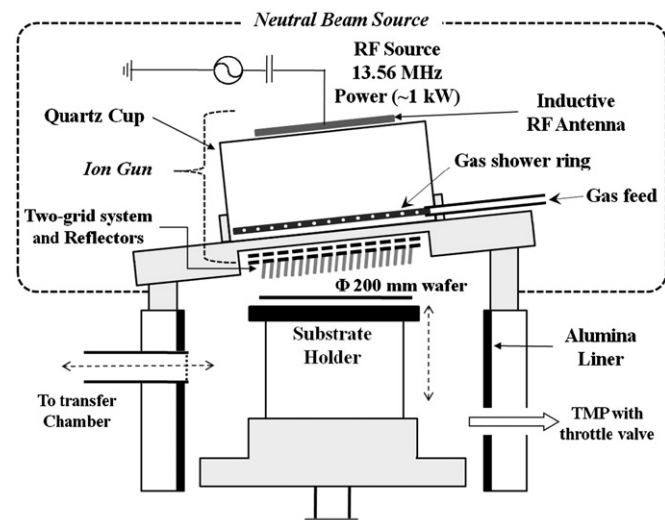

Fig. 1. Schematic diagram of the neutral beam deposition system used in the experiment.

the gas mixture, 10 sccm of an inert gas such as Ne, Ar, or Xe was added to change the characteristics of the deposited film. Corning 1737 glass was used as the substrate and the substrate temperature was kept at room temperature. The operating pressure in the processing chamber was varied from 10 to 40 mTorr and at the first grid of the two-grid system, a voltage of up to 500 V was applied to supply energy to the extracted ions, while the second grid was grounded.

Raman spectroscopy (Kaiser Optical System Inc.) was used to evaluate the crystalline volume fraction of the films with a deposition thickness of 180 nm. The deposited film thickness was measured by a surface profilometer (Tecor, Alpha step-500). The detailed microstructures of the deposited thin film, such as the grain size, were observed by using the high resolution transmission electron microscopy (HRTEM, JEOL JEM 3000F). The dark conductivity of the 180 nm thick films deposited as a function of the additive gas at different first grid voltages was investigated by a semiconductor characterization system (Keithley 4200) after the formation of Al coplanar electrodes on the deposited nc-Si:H.

3. Results and discussion

The deposition rate of the film in the neutral beam deposition system is influenced by several external process parameters such as rf power of the ICP ion gun, process pressure, gas composition, etc. In this experiment, SiH_4 was diluted with H_2 for the deposition of nc-Si:H [11] and the pressure of the process chamber containing SiH_4/H_2 and inert gas species with different atomic masses, viz. Ne, Ar or Xe, added to the SiH_4/H_2 was varied and its effect on the deposition characteristics was investigated. Fig. 2 represents the effect of the process pressure and the first grid voltage on the deposition rate of nc-Si:H for SiH_4-based gas combinations. As the gas combination, SiH_4 diluted with 80% H_2 was used and in the gas mixture, an additive gas, viz. Ne, Ar or Xe, was added at an amount corresponding to about 10% of the total gas flow rate of 100 sccm. In Fig. 2(a), the deposition rates measured as a function of operating pressure varied from 10 to 40 mTorr while the first grid voltage was maintained at 500 V, as are shown. In Fig. 2(b), the deposition rates measured as a function of the first grid voltage from 100 to 500 V at 20 mTorr of operating pressure without the addition of the inert gas [SiH_4 (10 sccm)/H_2 (90 sccm)] and with the addition of Ar [Ar (10 sccm)/SiH_4 (10 sccm)/H_2 (80 sccm)] are shown. As shown in Fig. 2(a), the deposition rate increased with increase in process pressure up to about 20 mTorr, which was controlled by changing the opening aperture size of the throttle valve or various additive gas conditions and further increase in the pressure saturated or slightly decreased the deposition rate. The initial increase of the deposition rate with increase in the process pressure is believed to be related to the increase in the number of radicals and ions with increase in operating pressure in the ICP source. Therefore, deposition rate is related to the increased flux of silicon species on the substrate. However, a slight decrease in the deposition rate with increase in pressure at pressures higher than 20 mTorr is believed to be related to the increased scattering of the ions reflected on the reflector surface. That is, when the ion beam was reflected on the reflector at pressures higher than 20 mTorr, more ions are scattered before the reflection on the reflector, resulting in the decrease of neutral beam flux to the substrate. Therefore, for the following experiments, a process pressure of 20 mTorr was applied.

When the deposition rate was measured with the addition of different inert gases, as shown in Fig. 2(a), it is seen that the addition of an inert gas and especially one with a higher atomic mass increased the deposition rate. The increase of the deposition
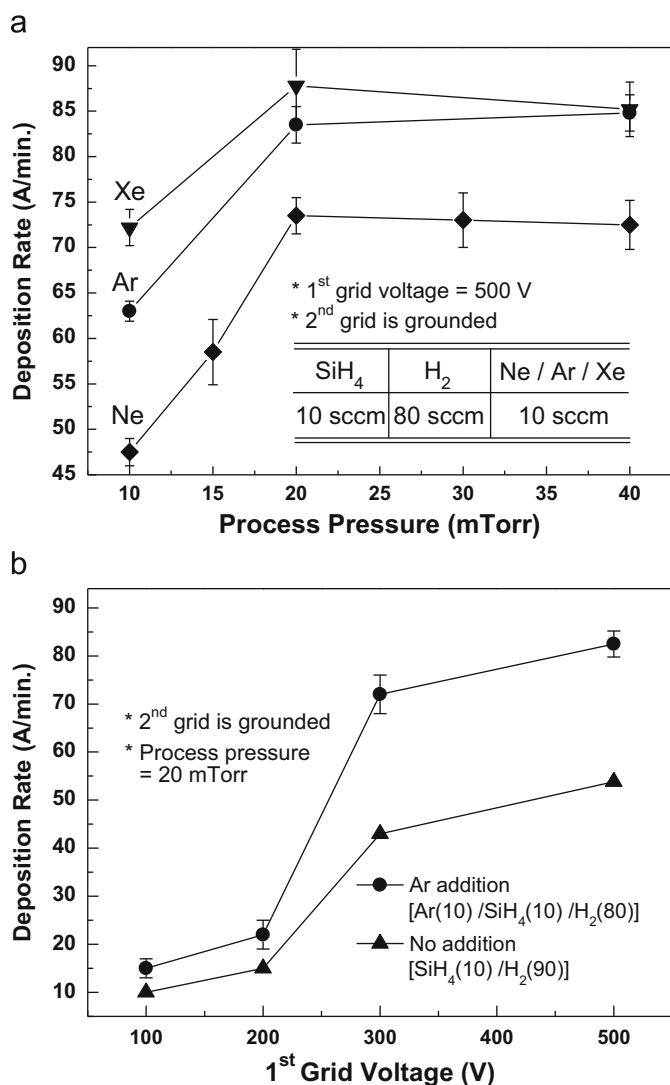
a

b

Fig. 2. (a) The deposition rates of nc-Si:H as a function of process pressure varied from 10 to 40 mTorr while the first grid voltage was maintained at 500 V for the various additive inert gas conditions. (b) The deposition rates of nc-Si:H at 20 mTorr as a function of the first grid voltage from 100 to 500 V without the addition of the inert gas and with the addition of Ar.

rate with the addition of the inert gas to the gas mixture of SiH_4/H_2 is believed to be related to the increased dissociative ionization of SiH_4 caused by the inert gas ions in the plasma through the charge exchange process and also to the increased surface activation by the increased energetic particles bombarding the surface caused by the enhanced plasma density in the ICP source. (The addition of an inert gas to the gas mixture of SiH_4/H_2 increases the plasma density in the ICP source, due to the high ionization probability of the inert gas atoms.) Charge exchange reactions occur in the plasma between neutrals and ions such as Ne and Ne^+, Ar and Ar^+, Xe and Xe^+, and these reactions can be represented by the following formula [12]:

$$A^{+(f)} + A^{(s)} \rightarrow A^{(f)} + A^{+(s)} \tag{1}$$

where (f) and (s) indicate fast and slow, indicating high and low kinetic energies, respectively. These reactions occur between an ion and the corresponding neutral, and are called symmetrical resonant charge exchange reactions. The ionization potentials of hydrogen (15.4 eV), neon (21.6 eV), argon (15.8 eV) and xenon (12.1 eV) are higher than that of silane (11.0 eV) as shown in Table 1 [13]. Therefore, the ion–molecule reactions of H_2^+, Ne^+,

Ar^+ or Xe^+ with silane result in the transfer of electron from silane to the ion [14], which can lead to dissociative ionization of silane. These are known as asymmetric charge exchange reactions resulting in SiH_x^+ ($0 \leq x \leq 3$) ions with thermal energy in the neutralizing system. The increase of the deposition rate for the inert gas with the higher mass is believed to be related to the increased plasma density for the inert gas with the higher mass due to the lower ionization potential, which enhances the charge exchange process and surface activation due to the improved plasma density in the ICP source.

As shown in Fig. 2, increase in the first grid voltage also increased the deposition rate, especially when the first grid voltage was increased from 200 to 300 V. Increase of the first grid voltage of the ICP ion source increases the energy of the particles bombarding the surface. Therefore, by supplying energy to the molecules adsorbed on the surface such as silane monomers and oligomers through the transfer of momentum, the resulting energetic particles are able to participate in the reactions as well as in pure chemical reactions. That is, the energetic particles incident on the surface influence the characteristics of the deposition process by forming a reactive region at the top most surface, while colliding with the surface. However, when the first grid voltage was higher than 300 V, even though the deposition rate was increased slightly, the deposited materials were damaged by physical bombardment.

The crystallization percentage of nc-Si:H deposited by the neutral beam with different additive inert gases, viz. Ne, Ar, and Xe, was estimated by Raman spectroscopy and is shown in Fig. 3. In the SiH_4/H_2 gas mixture, 10% of Ne, Ar, or Xe was introduced while the other process parameters, viz. the process pressure, rf source power, the first grid voltage, were maintained the same i.e. at 20 mTorr, 500 W, and 500 V, respectively. The Raman spectrum of the nc-Si:H film deposited at a first grid voltage of 300 V with the addition of Ar is also shown (thin line). As shown in Fig. 3, the deposited films were incompletely crystallized since the spectra exhibit two combinations, first a broad band, centered at around $480 \, cm^{-1}$, due to the amorphous silicon portion, and second, a peak near $520 \, cm^{-1}$ (more exactly, near 510 and $518 \, cm^{-1}$) corresponding to the crystalline portion. As shown in these spectra, a change in the additive gas changed the crystallization percentage and the use of an additive inert gas having a higher atomic mass improved the crystallinity of the deposited nc-Si:H film. It has been reported that Xe bombardment is more effective than Ar bombardment, which is generally used in PECVD, in enhancing the film quality [15,16]. This is related to the large mass of Xe as discussed previously in Fig. 2. Also, Xe has a low probability of penetrating into the silicon lattice, due to its large radius, resulting in less damage to the silicon crystal. Furthermore, the concurrent bombardment by a higher mass inert gas can activate the surface layer, thereby allowing the critical activation energy barrier to be exceeded, and increase the surface migration of the deposited silicon atoms. That is, the increase of the crystallinity with increase in mass of the additive gas appears to be related to the increase of the surface atomic mobility afforded by the
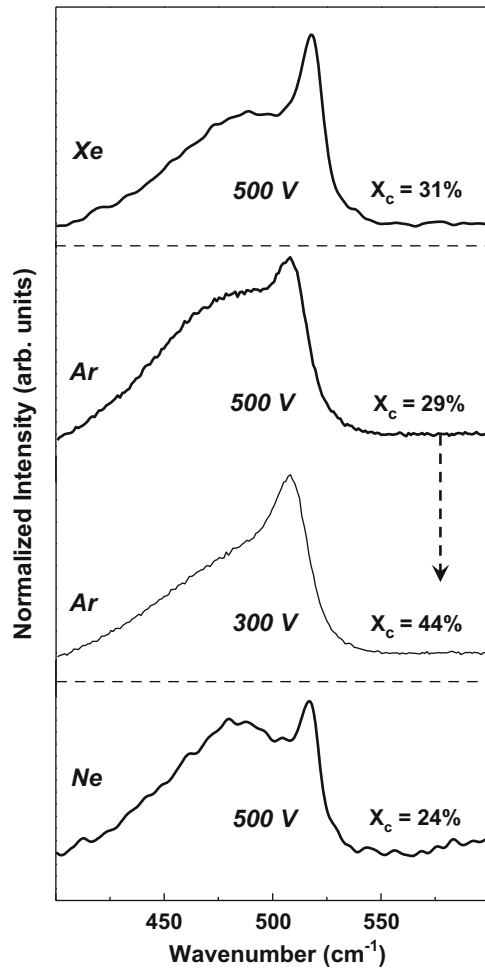
Fig. 3. Raman spectra of nc-Si:H films deposited with the LTNBD method, for several additive inert gas and first grid voltage combinations. A broad band centered at 480 cm^{-1} is α-Si portion and the narrow peaks centered near 510 and 518 cm^{-1} are c-Si portion. (Bold lines represent the first grid voltage of 500 V. And thin line is for the first grid voltage of 300 V.)
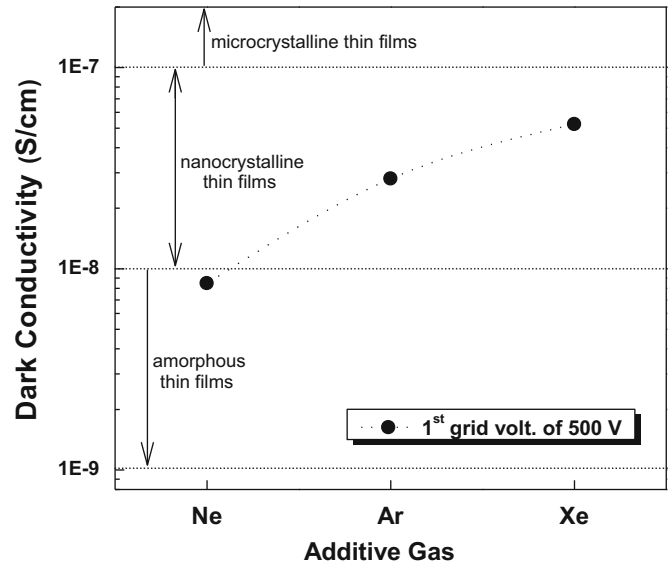

Fig. 4. Dark conductivity of the deposited nc-Si:H films for three additive inert gases.
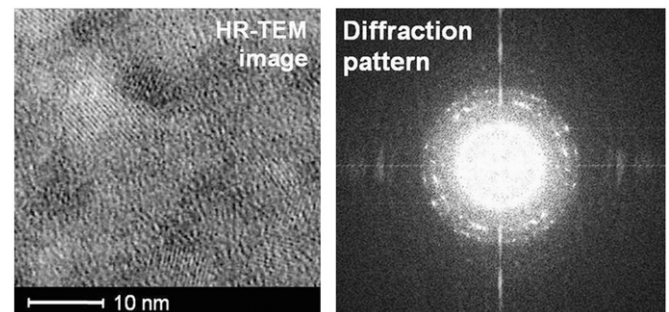

Fig. 5. HR-TEM micrograph and diffraction pattern image of the deposited nc-Si:H film at the condition of 300 V of first grid voltage and Ar addition ($X_c = 44\%$).

increased momentum transfer by the energy of the bombarding particles. As a result, the use of an additive gas and the use of one with a higher mass not only increased the deposition rate but also improved the crystallinity of the deposited film. Decreasing the first grid voltage from 500 to 300 V in the case of Ar addition improved the crystallization percentage significantly from 29% to 44%, indicating that the damage to the grown thin film was decreased at the lower particle bombarding energy.

The dark conductivity of the deposited nc-Si:H films [17–20] was measured by a semiconductor characterization system as a function of the additive inert gas at the first grid voltage of 500 V and the results are shown in Fig. 4. As shown in this figure, the use of a higher mass inert gas as the additive gas increased the dark conductivity from 8×10^{-9} S/cm for Ne to 5×10^{-8} S/cm for Xe, resulting in an increase of the crystallinity of the deposited nc-Si:H. The dark conductivity of the investigated film was in the conductivity range corresponding to nano-crystalline films.

To identify the crystal structure of the deposited silicon film, HRTEM was used. The micrograph of the silicon film deposited in our experiment with a first grid voltage of 300 V and Ar addition is shown in Fig. 5. As shown in this figure, nc-Si:H having a grain size of about 10 nm embedded in the α-Si:H could be observed. Therefore, an nc-Si:H structure was obtained by the neutral beam deposition of silicon at a low substrate-temperature (< 80 °C)

without a heating process. From the diffraction pattern, its nano-crystalline structure was also confirmed.

4. Conclusions

In this study, we investigated the possibility of depositing nc-Si:H film at a low temperature (< 80 °C) using a neutral beam. By varying the neutral beam energy and adding various inert gases to a gas mixture of SiH$_4$/H$_2$, nc-Si:H films having different crystallization volume fractions were obtained.

(i) The use of an additive gas, especially one with a higher mass, not only increased the deposition rate but also improved the crystallinity of the deposited film, due to the increase of the surface atomic mobility afforded by the increased momentum transfer.

(ii) The nano-crystalline structure of the deposited film having a grain size of about 10 nm was confirmed by the HRTEM micrograph.

(iii) Increasing the first grid voltage, that is, increasing the neutral beam energy, increased the deposition rate, but decreased the crystalline volume fraction.

Acknowledgment

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