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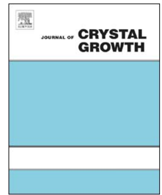

Low temperature deposition of polycrystalline silicon thin films on a flexible polymer substrate by hot wire chemical vapor deposition

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ABSTRACT

For the applications such as flexible displays and solar cells, the direct deposition of crystalline silicon films on a flexible polymer substrate has been a great issue. Here, we investigated the direct deposition of polycrystalline silicon films on a polyimide film at the substrate temperature of 200 °C. The low temperature deposition of crystalline silicon on a flexible substrate has been successfully made based on two ideas. One is that the Si–Cl–H system has a retrograde solubility of silicon in the gas phase near the substrate temperature. The other is the new concept of non-classical crystallization, where films grow by the building block of nanoparticles formed in the gas phase during hot-wire chemical vapor deposition (HWCVD). The total amount of precipitation of silicon nanoparticles decreased with increasing HCl concentration. By adding HCl, the amount and the size of silicon nanoparticles were reduced remarkably, which is related with the low temperature deposition of silicon films of highly crystalline fraction with a very thin amorphous incubation layer. The dark conductivity of the intrinsic film prepared at the flow rate ratio of $R_{HCl}=[HCl]/[SiH_4]=3.61$ was 1.84×10^{-6} Scm^{-1} at room temperature. The Hall mobility of the n-type silicon film prepared at $R_{HCl}=3.61$ was 5.72 $cm^2 V^{-1}s^{-1}$. These electrical properties of silicon films are high enough and could be used in flexible electric devices.

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1. Introduction

Low temperature fabrication of polycrystalline silicon thin films has attracted much attention for their potential applications in electric devices such as active matrix organic light-emitting diodes (AMOLED), high mobility silicon thin film transistors (TFT) and thin film solar cells [1–4]. Recently, electric devices based on polycrystalline silicon thin films are fabricated on a flexible substrate. The use of a flexible substrate may lead to more conformal, lightweight, portable, and inexpensive manufacturing [5–8]. A polyimide film is one of the most promising polymer substrate for flexible electronic devices such as flexible displays and flexible solar cells [5–7,9,10]. It is a high performance polymer which combines excellent physical, electrical, and mechanical properties with high glass transition temperature (T_g) around 350 °C.

Usually, silicon films deposited on glass or polymer at low temperature by plasma enhanced chemical vapor deposition (PECVD) or hot wire chemical vapor deposition (HWCVD) are amorphous or microcrystalline. Furthermore, an amorphous silicon called amorphous incubation layer (AIL) is inevitably deposited at the initial growth stage [11,12]. Because of this AIL formation, polycrystalline silicon films on a glass or flexible substrates have been usually prepared by the two-step process. First, amorphous silicon thin films are deposited on the substrate at low temperature. And then, crystallizing them by metal induced crystallization (MIC) [13–16], excimer laser annealing (ELA) [7,17,18] and rapid thermal annealing (RTA) [19]. Since these two-step processes increase the manufacturing cost and time of electrical devices, it is necessary to develop a direct deposition method of silicon films with high crystalline fraction.

Recently, Chung et al. [20–23] and Lee et al. [24] reported that the polycrystalline silicon films could be deposited on a glass substrate without post-treatment. It was possible to deposit polycrystalline silicon films without AIL by adding an appropriate amount of HCl gas during HWCVD based on two ideas. One is that the addition of HCl makes the retrograde solubility of silicon in the gas phase in the Si–H–Cl system. The other is that most films grow by the building block of nanoparticles generated in the gas phase during the CVD process [22].

The crystal growth by the building block of nanoparticles is a relatively new concept and called non-classical crystallization,

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which has been extensively studied for the past decade [25–31]. Non-classical crystallization is in contrast with the classical crystallization where individual atoms or molecules are the building unit. Recently, the crystal growth by nanoparticles in solution was directly observed by transmission electron microscopy (TEM) using a liquid cell technique [32–34]. According to a non-classical crystallization, many crystals that were believed to grow by atomic, molecular or ionic entity may actually grow by nanoparticles. Cölfen and Antonietti [35] made an extensive review on non-classical crystallization. Much earlier Sunagawa [36,37] made a similar suggestion that the growth unit of synthetic diamond is not an atom but a much larger unit.

More recently, a similar concept has been suggested in the PECVD process by Cabarrocas [38,39] Vladimirov and Ostrikov [40], and Nunomura et al. [41]. In the silane plasma CVD process, the incorporation of crystalline silicon nanoparticles into the films produced a so-called polymorphous structure [36,37]. Moreover, the building block of nanoparticles is utilized to synthesize various nanostructures by the plasma-aided nanofabrication [40,41]. In the non-plasma process such as thermal and hot wire CVD (HWCVD), Hwang et al. [42–56], extensively studied non-classical crystallization of thin films and nanostructures. They emphasized that the presence of charge in the nanoparticles plays a critical role in the evolution of dense films, which means that neutral nanoparticles would produce porous aggregations [57]. The generation of charged nanoparticles (CNPs), which was predicted to form in the gas phase during CVD, was experimentally confirmed not only in the Si CVD process [54,56,58,59] but also in many other CVD processes [48,53,56,60].

In this work, we deposit polycrystalline silicon films on the polyimide films by HWCVD based on the understanding that the Si–H–Cl system has a retrograde solubility and the films grow by the mechanism of non-classical crystallization. For the microstructural verification of retrograde solubility, the effect of HCl addition on the precipitation of silicon was examined by capturing the silicon nanoparticles on the transmission electronic microscopy (TEM) grid membrane. Crystalline silicon could be deposited with very thin 2–3 nm AIL on the polyimide film substrate. By approaching the film deposition by the new concept of non-classical crystallization and the thermodynamic information on the retrograde solubility of the Si–Cl–H system, polycrystalline silicon films with a minimal thickness of AIL could be directly deposited on the polymer substrate. Moreover, deposited films have high electrical properties suitable for flexible application.

2. Experimental details

Polyimide (Kapton® Type HN, Dupont) was used as a substrate for deposition of silicon films by HWCVD. The size of the square polyimide substrate is 2.5 cm × 2.5 cm. Tungsten filaments with a diameter of 0.5 mm and a length of 22 cm were used as hot wires. The filaments were heated resistively by a DC power supply. The distance between the substrate and filament was 4 cm. The films were deposited at filament and substrate temperatures of 1800 °C, and 200 °C, respectively, under 0.1 Torr. The filament and substrate temperatures were measured respectively by an infrared optical pyrometer (marathon, Raytek, USA) and a thermocouple in contact with a substrate controlled with a self-regulating heating system.

Hydrogen diluted silane and phosphine gases such as 70% $H_2-30\%SiH_4$ (SiH_4, 99.9999%, Wonik materials, Korea) and 95% H_2-5% PH_3 (99.9999%, Air liquid, Japan) were used as precursors. A varying amount of HCl gas (99.999%, Tsurumi Soda, Japan) was supplied additionally. The flow rate of each precursor was controlled by a mass flow controller (MFC, Tylan, USA). During the process, the reactor pressure, monitored by a baratron gauge (626A12TBE, MKS, USA), was maintained at 0.1 Torr by the pressure controller (651C, MKS, USA) equipped with a throttle valve.

The flow rate of H_2 diluted SiH_4 was fixed at 12 standard cubic centimeters per minute (sccm) in all deposition conditions. The HCl concentration was controlled by the ratio of HCl to SiH_4 designated as $R_{HCl}=[HCl]/[SiH_4]$, where the bracket represents the flow rate. It should be noted that $[SiH_4]$ represents the flow rate of pure SiH_4, not H_2 diluted SiH_4. Similarly, the doping concentration was controlled by the ratio of PH_3 to SiH_4 designated as $R_{PH_3}=[PH_3]/[SiH_4]$.

The silicon film thickness was measured by the surface profile of Alpha-Step IQ (Rev. AL-1). The crystallinity of the films at different R_{HCl} was analyzed by Raman spectroscopy (JobinYvon, LabRam HR Raman spectrometer). In order to prevent thermal crystallization by an incident laser beam of Raman spectroscopy, the power of Ar ion laser (514.532 nm) was kept below 0.05 mW. To confirm the existence of the silicon gas phase nuclei, Cu grids with a silicon monoxide membrane for transmission electron microscopy (TEM, JEM-3000F, JEOL, Japan) observation were used to capture the gas phase nuclei for 10 s using a shutter covering the grid membrane during HWCVD. To examine the effect of HCl on the number density and crystallinity of these gas phase nuclei, the capture was done at $R_{HCl}=0$, 1.39, and 3.61. The cross-sectional microstructure of the polycrystalline silicon films was prepared using a focused ion beam (FIB, Nova 200, FEI, USA) and observed by field emission scanning electron microscopy (FESEM). Then, the specimens were observed by high resolution TEM (HRTEM, F30, FEI, USA) operated at 300 keV.

To examine the effect of HCl on the dark conductivity of the films, R_{HCl} was varied at 0, 0.56, 1.39, 2.50, and 3.61. The dark conductivity of the intrinsic silicon films of 250 nm thickness was measured using a probe station (MST-6000C, MS Tech, Korea) with an analyzer (4145B, Agilent-HP, USA) in the range of 25–225 °C with an interval of 40 °C after depositing a coplanar aluminum electrode on the top of the film. For the Hall mobility measurement of PH_3 doped n-type silicon films of 250 nm thickness, the PH_3 concentration was varied with $R_{PH_3}=0.005$, 0.009, 0.014, 0.021, and 0.028. Samples of 1 cm × 1 cm with four silver contacts at each corner were placed in a dark chamber under a magnetic flux of 0.5 T in a Hall measurement apparatus (HL 5500, Nanometrics, USA) using a van der Pauw technique at room temperature [61].

3. Results and discussion

Fig. 1 show the silicon film deposited on the polyimide by HWCVD. During the deposition, the polyimide substrate did not have a thermal damage without any crack or delamination detectible by naked eyes even after bending the films as shown in Fig. 1. To distinguish between deposited and non-deposited areas, one corner of the polyimide was covered by glass. This corner is the bright area indicated by the arrow in Fig. 1, which is distinguished from the other deposited area by contrast.

Fig. 2 shows Raman spectra of silicon films deposited at various R_{HCl}. The thickness of films is 250 nm. The Raman spectra consist of three peaks: amorphous phase at 480 cm^{-1}, microcrystalline phase around 505–515 cm^{-1}, and crystalline phase at 520 cm^{-1} [60,62]. With increasing R_{HCl}, the peak of the amorphous phase decreased gradually. At $R_{HCl}=3.61$, which is the maximum value, the peak of the amorphous phase is almost absent and only a tiny peak of the microcrystalline phase remained. These results clearly show that the crystallinity of the films increased with increasing HCl concentration.

Fig. 3 shows the dependence of the growth rate (R_d) and the crystalline volume fraction (X_c) of the films on R_{HCl}. R_d decreased

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