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Non-classical crystallization of silicon thin films during hot wire chemical vapor deposition

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ABSTRACT

The deposition behavior of silicon films by hot wire chemical vapor deposition (HWCVD) was approached by non-classical crystallization, where the building block of deposition is a nanoparticle generated in the gas phase of the reactor. The puzzling phenomenon of the formation of an amorphous incubation layer on glass could be explained by the liquid-like property of small charged nanoparticles (CNPs), which are generated in the initial stage of the HWCVD process. Using the liquid-like property of small CNPs, homo-epitaxial growth as thick as ~150 nm could be successfully grown on a silicon wafer at 600 °C under the processing condition where CNPs as small as possible could be supplied steadily by a cyclic process which periodically resets the process. The size of CNPs turned out to be an important parameter in the microstructure evolution of thin films.

1. Introduction

There have been increasing experimental evidences indicating the crystal growth by the building block of nanoparticles, which is called ‘non-classical crystallization’ [1–5]. Recently, non-classical crystallization was directly observed by in-situ transmission electron microscope (TEM) observations using a liquid-cell technique [6,7]. Although non-classical crystallization is a relatively new and revolutionary concept, it has now become so established that several review papers [8–10] and a few books [11,12] have been published and its tutorial and technical sessions were included respectively in the spring meetings of Materials Research Society (MRS) and European Materials Research Society (EMRS) in 2014. With the establishment of non-classical crystallization, many crystals that were believed to grow by atomic, molecular, or ionic entities turn out to grow actually by nanoparticles.

Hwang et al. [13–17] studied extensively the non-classical crystallization in the chemical vapor deposition (CVD) process. They suggested that the electric charge carried by the nanoparticles played a critical role, by which the non-classical crystallization of thin films and nanostructures by the building block of nanoparticles is made possible. Because of the critical role of charge, they called this new growth mechanism in the gas phase synthesis ‘theory of charged nanoparticles (TCN) [16]. According to this theory, charged nanoparticles (CNPs), which are spontaneously generated in the gas phase in most CVD processes, crystallize as thin films and nanostructures. If nanoparticles are neutral, they undergo random Brownian coagulation, producing a very porous structure. If they are charged, however, they deposit as dense films, not leaving voids behind. This is attributed to the property of CNPs, which undergo self-assembly and are liquid-like, resulting in epitaxial recrystallization. They suggested that small CNPs are more liquid-like than large ones because the number of atoms per charge increases with increasing size of CNPs for the same amount of charge [16,17]. The liquid-like property of small CNPs was deduced from the experimental observations that dense crystalline films are produced by the deposition of CNPs whereas porous skeletal structures are produced by the deposition of neutral nanoparticles. Besides, it was also observed that the crystalline quality increases with decreasing size of CNPs. These results imply that the bonding strength of nanoparticles might be weakened by the presence of charge. Indeed, the ab initio study of the charge effect on the bond strength by Clare et al. [18] showed that the charge weakens the bond strength.

The concept of non-classical crystallization in the gas phase synthesis of thin films can explain many puzzling phenomena [16,17], which could not be explained by classical crystallization. For example, the TCN could successfully explain the paradoxical experimental observation of simultaneous deposition of less stable diamond and etching of stable graphite [13,16]. This phenomenon violates the second law of thermodynamics if approached by the classical concept of

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crystal growth by an atomic unit. The TCN could also explain the puzzling phenomena that a diamond film deposits on a silicon substrate whereas a porous skeletal soot structure deposits on an iron substrate under the same processing condition [14,19].

Therefore, it is necessary to approach many puzzling phenomena, which have not been understood clearly by the classical concept of crystal growth, by the concept of non-classical crystallization. For example, an amorphous incubation layer (AIL) tends to be formed on glass before microcrystalline silicon starts to deposit by hot wire CVD (HWCVD) and plasma enhanced CVD (PECVD) [20–23]. The formation of AIL, which has the thickness of several tens to a few hundreds of nanometers, is critically harmful when the low temperature deposition of crystalline silicon is applied to electric devices such as thin film transistors (TFTs) and solar cells. The formation mechanism of AIL can be approached by the TCN. Chung et al. [24] reported that the size of CNPs in the gas phase increased with deposition time up to 15 min in the silicon HWCVD process. Since CNPs formed in the early stage of deposition are so small that they are liquid-like and they tend to accommodate their structure to the amorphous structure of the glass substrate. As a result, the AIL is formed in the initial stage of deposition. As the deposition process goes on, CNPs grow larger in the gas phase and become less liquid-like. Then, they tend to maintain their structure after deposition instead of changing their structure to that of the substrate or the growing surface. This is why the AIL is formed in the initial stage of deposition and the microcrystalline silicon structure is formed in the later stage.

The liquid-like property of CNPs also depends on the substrate temperature. For the same size, CNPs can be more liquid-like at the high substrate temperature and less liquid-like at the low substrate temperature. Therefore, in order to reduce or remove the AIL on glass, the initial deposition condition should be made in such a way to make CNPs as least liquid-like as possible by increasing their size or decreasing the substrate temperature. On the other hand, the liquid-like property of small CNPs would be favorable for epitaxial growth. In order to enhance the epitaxial growth, the deposition condition should be made in such a way to make CNPs as liquid-like as possible by decreasing their size or increasing the substrate temperature. Therefore, the deposition behavior of CNPs would depend critically on their size as suggested by Jung et al. [25]. In this paper, the deposition behavior of CNPs will be studied focusing on their size effect.

2. Experimental details

Silicon thin films were deposited using an HWCVD reactor, where three linear tungsten filaments were aligned in parallel. The distance between the substrate and filament was 2 cm. The temperatures of the filament and substrate were measured respectively by an infrared optical pyrometer and the direct contact of a thermocouple with the substrate. The substrate temperature was controlled with a self-regulating heating system. The filament and substrate temperatures were respectively 1800 °C and 300 °C. The reactor pressure was 13.3 Pa. The flow rate of each precursor and gas was controlled by a mass flow controller (MFC, Tylan). Hydrogen (H_2) diluted 30 vol% silane (SiH_4 99.9999%, Wonik materials), and 5 vol% phosphine (PH_3, 99.9999% Air liquid) gases were used as a precursor for n-type doping to measure the electrical property. The flow rates of H_2 diluted SiH_4, H_2 diluted PH_3 and H_2 were fixed at 5 sccm, 1.6 sccm and 12 sccm, respectively. To improve the crystallinity of films, 24 sccm of HCl (99.999% Tsurumi Soda) was supplied [26–28].

To examine the deposition behavior which depends on the size of CNPs, n-type silicon films were deposited on a Corning Eagle XG glass. To observe the cross-sectional microstructure of the silicon films, TEM specimens were prepared using a focused ion beam (FIB, Nova 200, FEI). The specimens were observed by high resolution transmission electron microscope (HRTEM, F30, FEI) operated at 200 KeV. The crystallinity of deposited film was measured by a Raman spectroscopy (LabRam ARAMIS, Horiba Jobin-Yvon) and the dark conductivity of films was measured using a four-point probe at room temperature. The thickness of films was measured by the surface profile of Alpha-Step IQ (Rev. AL-1).

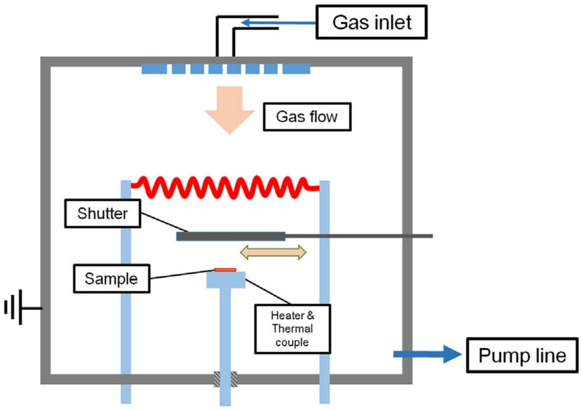

Fig. 1. Schematic of experimental set-up of the HWCVD reactor.

In order to control the size of the nanoparticles formed in the gas phase in the initial stage of deposition, the delay time was used as a processing parameter. To control the delay time before deposition, a shutter, which covers a substrate and thereby isolates it from the reactor environment, was installed above the substrate as schematically shown in Fig. 1. The delay time means the amount of time duration that the shutter covered a substrate after the filaments were heated up in the HWCVD process.

To confirm how the size of nanoparticles formed in the gas phase varies with delay time, the nanoparticles were captured for 10 s on a carbon membrane of the TEM Cu grid using a shutter after delay times of 0, 5 and 15 min and observed by TEM. To examine the effect of the size of nanoparticles on the deposition behavior, it is necessary to deposit the relatively uniform size of nanoparticles. However, the size of nanoparticles continues to increase with processing time until it reaches a steady state value after ~15 min in this process of HWCVD. For this reason, it is not possible to deposit films exclusively with small nanoparticles which are generated in the initial stage of deposition.

In order to deposit films exclusively with small nanoparticles which are generated in the gas phase for the first 30 s after the filament was heated up, the deposition was done only for 30 s and then the substrate was covered by the shutter. Then, the power supply of the filament was turned off and the supply of the gas flow was stopped. This is the one cyclic process. After 10 min, the filament was heated up again and the gas flow was supplied again. After this, the shutter was removed from the substrate for another 30 s deposition. By 6 cyclic processes of this way of deposition, which corresponds to 180 s or 3 min of net deposition, we could deposit the film exclusively with the small nanoparticles, which are generated for the first 30 s of the HWCVD process.

The deposition behavior was compared among four different process conditions as shown in Fig. 2. In the deposition condition of Fig. 2(a), the film was deposited for 180 s without delay time, which corresponds to the normal deposition. In Fig. 2(b), the film was deposited for 180 s after the delay time of 5 min. In Fig. 2(c), the film was deposited for 30 s after the delay time of 5 min and the cyclic deposition process was repeated 5 times with the total deposition time being 180 s. In Fig. 2(d), the film was deposited, without delay time, by 6 repeated cyclic depositions with the total deposition time being 180 s. In Fig. 2, the delay time, which was to control the size of nanoparticle at the initial stage of deposition, should be distinguished from the time between cycles, which was to initialize the process with a purpose of minimizing the size of nanoparticles.

In order to examine the size effect of nanoparticles on the homo-