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Journal of Organometallic Chemistry 611 (2000) 531–536

Journal of Organo metallic Chemistry

Low-temperature growth of polycrystalline Si and Ge films by redox reactions of Si_2H_6 and GeF_4

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Received 3 March 2000; accepted 26 March 2000

Abstract

Low-temperature growth of polycrystalline Si and Ge films has been investigated by low-pressure chemical vapor deposition (LP-CVD) featuring a redox reaction of disilane (Si_2H_6) and Germanium tetrafluoride (GeF_4). The film growth is established in a wide range of 0.4–100 torr and in low-temperature range of 300–450°C. The Si content significantly depends on the reaction modes in which either Si_2H_6 or GeF_4 is activated preferentially, and thus the film composition is varied from >90 atm% Si to >90 atm% Ge. It is found that the isolated nuclei are formed directly on the substrate surface and provides a good basis of high crystallinity in a thin film irrespective of the film contents. The mechanism of film growth and the origin of low-temperature crystal growth are discussed from a chemical point of view according to the experimental results. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Germanium tetrafluoride; Disilane; Thermal CVD; Polysilicon; Crystal growth

1. Introduction

Nowadays, the hydrogenated amorphous silicon (a-Si:H) thin film prepared by rf-grow discharge of silane (SiH_4) is established for large-area electronic devices such as thin film transistors (TFTs) for liquid crystal displays, solar cells, and xerographic photoreceptors for copiers and laser printers. The a-Si:H films, however, remains a serious problem of photo-induced degradation of electrical properties [1], and basically can not provide us with high mobility over 10 $cm^2\ V^{-1}\ s^{-1}$ due to the amorphous nature [2]. Thus, a new material is required for advanced large-area electronic devices such as TFT arrays with driving circuits for low-cost and high performance display devices and stacked thin film solar cells for power generation.

Polycrystalline Si (poly-Si) films prepared at a temperature where glass substrates are readily employed are a promising candidate for such advanced large-area electronic devices, because of a good compatibility with conventional Si device fabrication processes and of superior electronic properties, e.g., high mobility, effective doping efficiency, and a large absorption coefficient in infra-red region compared with the a-Si:H thin films.

Several preparation techniques for low-temperature growth of poly-Si have been proposed, which include plasma CVD [3], Hot-wire CVD [4], and photo-CVD [5]. Within these techniques, however, remain some problems to be solved: the crystallinity is poor at an early stage of film growth, resulting in inhomogeneous crystallinity and a low crystal fraction; high crystallinity and high rate growth hardly go together. The former is attributed to delayed nuclei formation during film growth and their competitive growth to the grains [6a,b] and the latter to the condensation of reactive species, ie., film precursors generated in the gas phase, resulting in powder formation. The latter problem is not so easy for us to solve in these conventional CVDs, because it is associated with a principle of their low-temperature film growth: high deposition rate requires high concentration of the precursors, resulting in their gas phase condensation.

To solve this dilemma, we have proposed a new principle for low-temperature growth of films without decomposing the source materials in the gas phase, i.e., reactive thermal CVD [7].

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PII: S0022-328X(00)00400-9

For poly-Si film growth, we selected disilane (Si_2H_6) and germanium tetrafluoride (GeF_4) as a set of the reactive source materials. Interestingly, we found that the crystal growth takes place at 450°C or less with compositional variety of Ge-rich to Si-rich and that isolated nuclei are formed directly on the SiO_2 substrate and the selective growth can be achieved by choosing growth parameters [8].

In this report, we will discuss the mechanism of film growth and the origin of low-temperature crystal growth from a chemical point of view on the basis of the experimental results.

2. Results and discussion

2.1. A new principal for low-temperature film growth

In order to reduce the growth temperature for film deposition in CVD processes, there are two approaches: one is to find out a new source material exhibiting a lower pyrolytic temperature: the other is to assist the decomposition of source materials with external energy. As far as the Si-related compounds are concerned, there are few materials with pyrolytic temperatures lower than those of SiH_4 (>500°C) and Si_2H_6 (>350°C) readily available. Therefore, the major effort to establish a low-temperature CVD process has been made in the latter approach.

In fact, in the low-temperature deposition of Si films, the source materials are decomposed at a certain region away from the heated substrate where the external energy is provided to excite the source materials for promoting their decomposition: in the plasma CVDs, for example, SiH_4 is decomposed in the plasma where accelerated electrons give kinetic energy to silane molecules, resulting in the dissociation of electronically excited silane molecules [9]; in the Hg-sensitized photo-CVD, photo-excited Hg atoms transfer their energy to silane molecules [10]; in hot-wire CVD, the heated W-filaments promote the decomposition of silane molecules [4]. In all these CVD processes, the reactive Si-related radicals are responsible for film growth at lower temperatures where the parent molecule, e.g., SiH_4 never decomposes so as to deposit the films.

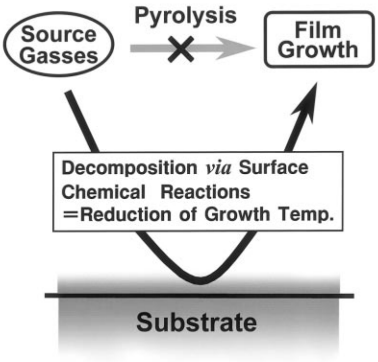

Fig. 1. Concept of reactive thermal CVD.

This principle, however, has a dilemma about the low-temperature film growth and high rate film growth for large-area applications, because the high concentration of the reactive species in the gas phase leads to powder formation. One of the solutions to solve this dilemma is to confine the reactive zone where the source materials are excited to decompose like the thermal CVD, in which the source materials are thermally activated to decompose in the vicinity of the heated substrate.

In a new principle, the redox reactions in a set of the source materials is featured to promote their decomposition leading to film growth as shown in Fig. 1. In fact, it was demonstrated in SiH_4–F_2 system that chemical reactions between SiH_4 and F_2 at the reduced pressure are effective to generate the reactive species and deposit Si films at 250°C [11]. This chemical process, however, can not escape from the above dilemma because of the spontaneous gas phase reactions of SiH_4 and F_2 at the ambient temperature. Thus, a new redox pair of source materials was chosen, i.e., Si_2H_6 and GeF_4, which can react with each other only when they are activated thermally or catalytically on the heated surface. In fact, the film deposition took place at heated substrate while no decomposition of these source gases is observed at the ambient temperature, which is confirmed by in-situ IR spectroscopy. [12]

For the metalization process in semiconductor technologies, W-CVD and its related processes [13] has been investigated, in which SiH_4 and WF_6 are used for the source materials. The basic concept of this film growth is very similar to the present principle, but it was not recognized well in such a manner described here.

2.2. Growth of Ge-rich films

In the combination of Si_2H_6 and GeF_4, there is a chance for Ge to be deposited when Si_2H_6 works as a reducing agent and is oxidized into stable final products such as SiF_4 and $SiHF_3$ without forming Si-related reactive intermediates on the surface and/or in its vicinity. In fact, it was found that Ge-rich (>90 atm%) films could be deposited very easily [14]. Interestingly, there was a peak at around 375°C in the deposition rate as a function of temperature as shown in Fig. 2. This indicates that there exist two film growth modes concerning film deposition. In the low temperature region of <400°C, epitaxial growth of Ge-rich film took place when Si (100) wafer was used even at the temperature

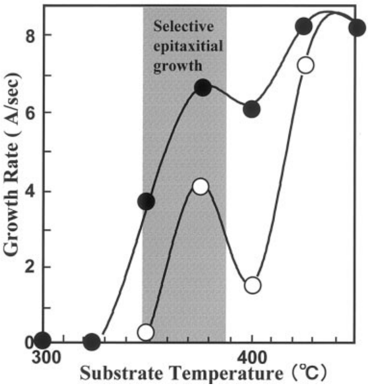

Fig. 2. Ge growth rate as a function of substrate temperature. GeF_4 flow rates were 1.5 (open circles) and 2 sccm (closed circles), while Si_2H_6 and He of dilutent gas flow rates were fixed at 30 and 300 sccm, respectively, and total pressure was at 1 Torr.

Fig. 3. SEM micrograph of Ge films selectively grown on Si surface on SiO_2-patterned Si substrate.

as low as 300–320°C. It should be noted that neither GeF_4 nor Si_2H_6 can be decomposed thermally in this temperature range. The crystallinity of the epitaxial films was degraded as the growth temperature was increased over 400°C. It turned out that this degradation is due to the nucleation of Ge crystallites while the grain growth takes place simultaneously. In a typical epitaxial growth of Si, the higher the growth temperature is, the better the crystallinity is established, because the crystal is the most stable form in thermal equilibrium condition.

It is well known that GeF_4 exhibits etching activity for Si. This fact indicates that GeF_4 is activated to be reduced probably into GeF_2 when absorbed on the Si surface. In fact, it was revealed from ESCA and in-situ IR measurements that very thin deposit of Ge (100–200°C) is formed on the Si wafer to which GeF_4 is exposed [15] and polymeric deposits of GeF_2, ie., $(GeF_2)_n$ is formed on the wall [12]. Therefore, it is plausible that GeF_4 is activated on the heated Si substrate when absorbed and results in being reduced easily into Ge in the presence of the reducing agent, Si_2H_6, even at the low temperature of 300°C where none of GeF_4 and Si_2H_6 are decomposed.

Interestingly, selective growth in which the film growth occurs only on bare Si surface and not on the SiO_2 [16] when SiO_2-patterned Si wafer was applied as a substrate as shown in Fig. 3. This fact provides us with a confirmation of the present idea, because no activation of GeF_4 results in no film deposition even at 375°C.

At a high temperature region over 400°C, non-selective growth took place, in which the film deposition occurred irrespective of substrate materials. In this regime, the continuous nucleation took place on the substrate surface at the initial stage of film growth and it enhanced when the reaction pressure was increased. This suggests that nucleation took place homogeneously, i.e., in the gas phase near the substrate surface. The final conclusion can not be drawn until what happens in the vicinity of the surface is clarified, but we speculate that thermally activated Si_2H_6 and GeF_4 could react each other in the gas phase near the surface, resulting in Ge cluster formation which leads to Ge nuclei on the surface.

As discussed above, it is concluded that two chemical mechanisms are concerned with the low-temperature growth of Ge-rich films: one is catalytic activation of GeF_4 on the surface, which makes it possible to selective and epitaxial growth of Ge-rich films; the other is thermal acceleration of reaction rate between GeF_4 and Si_2H_6, which leads to non-selective polycrystalline growth. In this film growth, the reaction pressure could be increased up to 100 Torr. This is one of good advantages over the plasma processes that can not be applied in such a high pressure, where it helps the substrate temperature keep uniform and reduces contamination from residual gas.

Interestingly, in polycrystalline growth of Ge, isolated nuclei were formed on the SiO_2 substrate without accompanying any amorphous tissue. Thus, with the combination of this nucleation and selective growth of resulting nuclei, the high crystallinity SiGe was prepared [17].

2.3. Growth of Si-rich films

As described in the previous section, Ge-rich film is easily deposited at the lower temperature, but it is difficult to increase Si content in the film when the substrate temperature was set below 450°C. The Si content was 20 atm% at most in spite of a large excess gas flow ratio of S_2H_6 against GeF_4, e.g. 7–8. It was found that Si content can be increased up to >90 atm% when the substrate temperature was increased over 450°C and a higher gas flow ratios over 10 were applied [17]. As is clear in Fig. 4, the Si content of films exceeds 95 atm%, which is estimated on the basis of Vegard's law from the X-ray diffraction peak of Si (220) in the film. As for the deposition rate, it was increased with an increase in the GeF_4 flow rate, but the normalized deposition rate with a given GeF_4 flow rate was almost constant in spite of the film contents. This fact indicates that GeF_4 plays the major role for film deposition even in the growth condition where the film is rich in Si. In this figure, the Ge content is increased very steeply when the GeF_4 gas flow rate was increased over 1.3 sccm. This characteristic behavior of this materials system should be related to the catalytic effect of Ge surface on the activation of source materials, i.e. GeF_4.

On the basis of the fact that the Si incorporation into the film significantly depends on the substrate temperature, we can point out that thermal activation of Si_2H_6 is an essential requirement to achieve effective Si incorporation into the films, so that the GeF_4 may help promoting not only the film growth but also structural relaxation of Si-network into the crystal growth. This will be discussed in more detail later on.

In this process, immediate and isolated nucleation took place on the SiO_2 surface as described in the Ge film growth. Furthermore, the selective growth was also realized by choosing the growth condition. Thus, the combination of this step by step process, the nuclei formation on the substrate and its selective growth to grains provided us with high crystallinity poly-Si-rich SiGe films at 450°C [18].

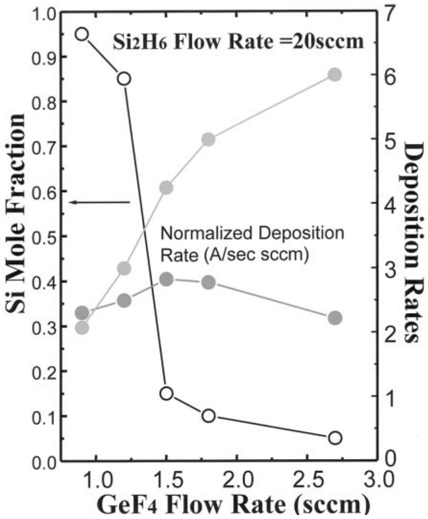

Fig. 4. Si-molar fraction and deposition rates of films as a function of GeF_4 flow rate. Si_2H_6 and He flow rates were fixed at 20 and 300 sccm, respectively. Total pressure was kept constant at 0.45 Torr.

2.4. Low-temperature crystal growth

The crystal growth of Ge is achieved at 350°C by the thermal CVD using GeH_4 as a source material [19]. In this process, the growth temperature of films is determined primarily by the pyrolytic temperature of GeH_4. It is well known that the bulk crystallization temperature of Ge is 400°C, so that it is natural that the crystal growth occurs at that temperature. However, it is not natural that the crystal growth of Si-rich film whose Ge content is less than 5 atm% occurs at the temperatures lower than 500°C, because incorporated Ge in 5 atm% or less does not change much in the crystallization temperature of films. In fact, the thermal CVD process for crystalline SiGe alloy requires high growth temperatures over 550°C when GeH_4 and Si_2H_6 were employed as source materials [20]. In addition, it should be noted that thermal decomposition of Si_2H_6 always afford amorphous films when the substrate temperature is lower than 500°C. Therefore, some specific mechanism of crystallization has to be associated with the present crystal growth of Si-rich films at 450°C.

The low-temperature crystal growth has been reported so far in various CVD processes including SiH_4–H_2 system with plasma [21] or hot W filaments, SiF_4–H_2 plasma systems [4], SiH_2Cl_2–H_2 plasma systems [22], and SiH_4–F_2 and Si_2H_6–GeF_4 reactive systems [11,17]. There are several mechanisms proposed for explaining the low-temperature growth of crystalline Si in each CVD process: Veprek et al. [23] discussed the plasma condition where the crystal growth takes place and proposed a chemical transport of Si in the equilibrium condition in the presence of atomic hydrogen; Tsai et al. [21] proposed preferential etching of amorphous tissue by atomic hydrogen for the crystal growth; Matsuda pointed out the importance of hydrogen coverage when the crystal growth takes place and explained that the hydrogen covered surface helps migrating the film precursors to find out the sites energetically favorable which leads to the crystal growth [24]. According to the fact that the film surface is covered with chlorine in the growth condition where the crystal growth takes place in SiH_2Cl_2–H_2 plasma [22], Matsuda et al. discussed this in terms of the effective migration of the precursors on the film surface.

In most of the CVD processes cited above, hydrogen plasma is associated with the film growth. Indeed all these explanation have a good basis for low-temperature crystal growth, but SiH_4–F_2 system is out of this discussion because of no atomic hydrogen incorporation in the crystal growth. Furthermore, the hydrogen coverage of the surface can not be expected in Si_2H_6–GeF_4 system because of high growth temperature over 400°C where thermal dissociation of H–Si bonds in the surface are activated.

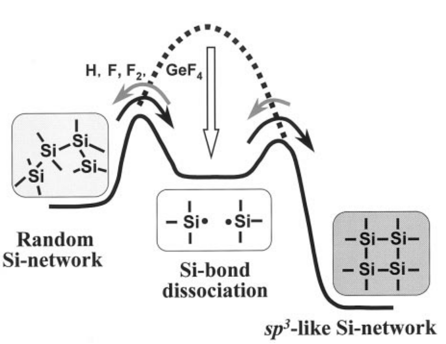

Fig. 5. Structural relaxation vs chemical equilibrium of Si-network. This illustrates an idea explaining the structural relaxation of Si-network into crystalline form via chemical equilibrium with the contribution of reactive species in the gas phase.

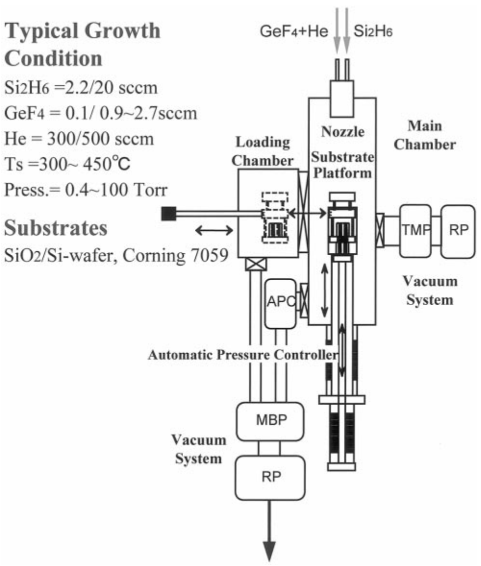

Fig. 6. Schematic diagram of LP-CVD apparatus and typical growth condition.

In a point of view that the crystal growth is a kind of the continuous propagation of relaxed Si-network where Si atoms are arranged in sp^3 configuration, the relaxation of Si-network at the initial stage of the film growth is very important for following network propagation. Once the Si-network is formed, it requires high temperatures above 600°C to transform it into the crystalline form. Therefore, in the low-temperature crystal growth there must be some specific dynamic chemical processes that rearrange Si-network into more stable sp^3-like configuration during the film growth.

As discussed in the proposed mechanisms for the low-temperature crystal growth, most of the above mentioned CVD processes involve the intensive contribution of atomic hydrogen, which exhibits etching activity for Si films, in the crystal growth. This is true in SiH_4–F_2 and Si_2H_6–GeF_4 systems as well in terms of the contribution of chemical species exhibiting etching activity, which are atomic fluorine, fluorine, or GeF_4. Therefore, one can recognize some contribution of these reactive species to the relaxation of Si-network during the film growth.

In the presence of chemical species that exhibit etching activity, the Si–Si bond formation and its kinetic dissociation occur simultaneously on the top surface during the film growth. Thus, the Si-network near the surface propagates in a kind of chemical equilibrium resulting from the contribution of the reactive species as schematically illustrated in Fig. 5. This idea can explain how the relaxation of Si-network takes place in all the CVD processes described above: in the processes where atomic hydrogen are involved, atomic hydrogen mediates this chemical equilibrium and promotes the rearrangement of Si–Si bonds, leading to thermodynamically stable Si-network, i.e., nucleation; in SiH_4–F_2 and Si_2H_6–GeF_4 systems, F_2 and GeF_4 mediate it and give the same result as in the case with atomic hydrogen, respectively. This is a speculation based on the common chemical reactivity of the reactive species involved in these CVD processes.

Therefore, further studies including in-situ analysis and chemical characterization of the film surface and gas phase products in these CVD processes, will give insight into the chemical equilibrium assumed. In fact, the growing surface is always covered with hydrogen when the crystal growth of Si takes place in silane plasma process as Matsuda pointed out. As the surface is covered with hydrogen, so it was done with chlorine in SiH_2Cl_2 plasma process when the crystal growth takes place. This can be a good sign for this idea because such a chemically equilibrated surface should be covered with the active species involved, i.e., H and Cl.

3. Experimental

The experimental apparatus used for film deposition is a typical cold-wall type of low-pressure CVD reactor as shown in Fig. 6. It consists of a main chamber equipped with a gas nozzle, a substrate platform, a loading chamber, and two vacuum systems for baking and deposition. The substrates, a piece of SiO_2/c-Si wafer, a quartz plate, and a Corning 7059 glass plate were set on the substrate platform equipped with a heater unit and their temperatures were monitored by a thermocouple and controlled at 450°C.

In a typical experiment, flow rates of source materials, i.e., Si_2H_6, GeF_4, and He as a dilutent were 2–20, 0.1–2.7, and 300–500 sccm, respectively, which were regulated by mass flow controllers. The reaction pressure was kept at 0.4–100 Torr by using an automatic pressure controller.

The film thickness was determined by scanning electron microscope (SEM). The film composition was estimated by Vegard's law from X-ray diffraction peak of Si (220) face. Structural properties of the films were determined by Raman and X-ray diffraction spectroscopies.

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