The microstructure evolution of hydrogenated microcrystalline germanium promoted by power gradient method

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ABSTRACT

This paper studies the microstructure evolution of hydrogenated microcrystalline germanium ($\mu\text{c-Ge:H}$) thin films deposited by plasma enhanced chemical vapor deposition (PECVD). There is an amorphous incubation layer formed in the initial deposition stage of $\mu\text{c-Ge:H}$ thin film. It is demonstrated that the thickness of incubation layer can be reduced by high hydrogen dilution and high discharge power method. However, at high hydrogen dilution, the deposition rate of $\mu\text{c-Ge:H}$ appears a sharply decrease. Using a high discharge power can compensate the deposition rate decrease but lead to decrease of average grain size and appearance of micro-void in the $\mu\text{c-Ge:H}$ thin film. In addition, by comparing two thickness groups of $\mu\text{c-Ge:H}$ thin films deposited at different discharge powers, it is noticed that the evolution process relates to the formation of crystal nucleuses. Thus, a power gradient method is proposed to understand the mechanism of nucleation and crystal growth in the initial deposition process of $\mu\text{c-Ge:H}$ films. Finally, by power gradient method, the incubation layer thickness of $\mu\text{c-Ge:H}$ thin films has been decreased to less than 6nm. Moreover, Raman scattering spectra shows a 38 nm $\mu\text{c-Ge:H}$ film has a crystal fraction

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(X_c) of 62.4%. Meanwhile, the mobility of TFT devices shows the improved electrical property of $\mu\text{-Ge:H}$ film deposited by power gradient method.

KEYWORDS: B2. Hydrogenated microcrystalline germanium; A3. Plasma enhanced chemical vapor deposition; A3. Power gradient method; A1. Nucleation; A1. Incubation layer; B3. Thin film transistors

1.Introduction

Hydrogenated microcrystalline germanium ($\mu\text{-Ge:H}$) thin films prepared by plasma enhanced chemical vapor deposition (PECVD) have a high optical absorption coefficient and a narrow optical gap closing to 0.66 eV [1,2]. This promises $\mu\text{-Ge:H}$ thin films can be widely used in narrow band gap photovoltaic devices and thin film transistors (TFTs) [3,4]. It was reported that the growth mechanism of $\mu\text{-Ge:H}$ thin films is basically similar to the hydrogenated microcrystalline silicon ($\mu\text{-Si:H}$) which has been extensively studied [5-9]. In the initial growth process, at first, a layer of amorphous germanium (a-Ge:H), called incubation layer, appears on substrate, and then crystalline grains appear and grow up. There is a region that amorphous structure gradually evolves into microcrystalline structure [10-12]. However, in this region, a thick incubation layer deteriorates all film and device performance. In the application of solar cells, since photo-generated carriers are transported along the growth direction in intrinsic layer, defects in incubation layer increase carrier recombination rate. Furthermore, when the film is thin, a high amorphous content causes electrical properties deteriorate and lead to TFT performance decrease.

In order to reduce incubation layer thickness and promote microstructure evolution, many methods have been adopted in $\mu\text{-Si:H}$ thin films studies, like high hydrogen dilution and two step growth methods [13-16]. A high crystalline volume fraction of $\mu\text{-Si:H}$ films was obtained by

using high hydrogen dilution, however, it caused a sharply decrease of the deposition rate simultaneously [17,18]. To further improve the crystalline fraction (X_C), two step deposition method [15] or named hydrogen plasma treatment method was studied. By using a film treated by H_2 plasma for few minutes as a seed layer, the film following deposited on this layer has a high crystalline fraction.

In this paper, we study the properties of initial deposition stage and the microstructure evolution of $\mu c\text{-Ge:H}$ films. At first, we show that the same as $\mu c\text{-Si:H}$, the high hydrogen dilution method is an effective method for reducing the incubation layer thickness of $\mu c\text{-Ge:H}$ thin films. And then, by comparing two thickness groups of $\mu c\text{-Ge:H}$ films deposited under different discharge powers, we find that a higher power can further promote the microstructure evolution and compensate the decrease of deposition rate caused by high hydrogen dilution. We illustrate the evolution of crystal fraction and surface morphology with the thickness increase of $\mu c\text{-Ge:H}$ films. Finally, a power gradient method is proposed to understand the nucleation mechanism. Furthermore, we find this method is helpful for further reducing the thickness of incubation layer and controlling crystalline fraction and average grain size to achieve a homogeneous distribution of the crystal grains. Meanwhile, TFTs are used to evaluating the electrical properties of $\mu c\text{-Ge:H}$ films since the mobility can be extracted from current-voltage characteristics.

2. Experimental details

All $\mu c\text{-Ge:H}$ samples were deposited on glass substrates (Corning 7059) in a six-chamber-cluster RF-PECVD system using a GeH_4 and H_2 gas mixture, at a total gas flow of 200 sccm, a chamber pressure of 1Torr and a temperature of 260 °C. The crystalline volume fraction and the microstructure evolution of $\mu c\text{-Ge:H}$ films were investigated by Raman scattering

spectroscopy, using an InVia Renishaw Raman system with a He-Ne laser excitation at 514.5 nm. The structural properties of $\mu\text{c-Ge:H}$ thin films were observed by transmission electron microscope (TEM). Atomic force microscopy (AFM Seiko SPA-400) was carried out to observe the surface morphology. X-ray diffraction measurements was carried out using a Philips X'pert Pro diffractometer with Cu-K α radiation at 45 kV and 40 mA. The electrical performance of the TFT devices was measured using a Keysight Technologies B1500A Semiconductor Device Analyzer. All devices were tested in air at room temperature.

The $\mu\text{c-Ge:H}$ samples (R199, R249, R499 and R999) prepared at different hydrogen dilution ratios ($R_H = [\text{H}_2] / [\text{GeH}_4]$) have a same thickness of 25 nm by controlling the deposition time. The groups of P05 and P35 were prepared at the RF discharge power of 5 W and 35 W respectively, and $R_H = 999$. Furthermore, another group (G1-G4) was prepared by the power gradient method. At first, a 3 nm initial layer was deposited at 35 W discharge power. And then, the power was turned down to 5 W in a short time (< 5 s) and kept plasma discharge continuous. At 5 W discharge power, the initial layer with crystal nucleuses followed deposition of different time. The TFT samples were prepared using 5 W, 35 W and power gradient method, to evaluate the electrical properties. The thickness of channel layer is 20 nm and the thickness of gate dielectric layer (SiO_2) is 270 nm.

3. Results and discussions

3.1 Effect of high hydrogen dilution

Fig. 1 shows the Raman spectra and TEM measurements of the group prepared under different hydrogen dilution conditions. Table 1 lists the deposition parameters. The Raman spectra shown in Fig. 1(a) indicates that with R_H increasing, there is a transition from amorphous to

microcrystalline phase. In Fig. 1(a), the crystalline fraction (X_C) is defined as the peak intensity ratio $X_C = (I_{300} + I_{295}) / (I_{300} + I_{295} + I_{275})$ [19]. It has been reported that using different laser wavelength, the penetration depth of Raman is different, and the penetration depth related to the absorption coefficient [20]. For the Ge films, the effective detection depth of 514 nm Raman laser is about 10 nm.

For the $\mu\text{c-Ge:H}$ films, with the same film thickness of 25 nm, a higher Raman crystalline fraction means the initial amorphous layer, or named incubation layer, is thinner. If crystal grains just form on the film surface, the thickness of incubation layer will be equal to the film thickness. It is about 25 nm for the incubation layer thickness of sample R249, but for sample R199 thickness is larger than 25 nm. Therefore, high hydrogen dilution is an effective method for decreasing amorphous incubation layer thickness and promoting microstructure evolution of $\mu\text{c-Ge:H}$ films at the same time. There are three different models to explain the role of hydrogen dilution in the formation of $\mu\text{c-Si:H}$ materials [21,22]. In the surface reaction models, it is important that the substrate surface is covered by hydrogen, on which film precursors diffuse more easily. In the growth zone models, the chemical annealing effect can provide energy for crystallization formation. Beyond that, since the deposition time for the high hydrogen dilution sample is longer, the in situ annealing effect can be another factor that promotes the crystallization of sample R999. Furthermore, it is noticed that there is an obvious downshift of crystal peak in Fig. 1(a). Sample R999 deposited at $R_H = 999$ presents a strong crystalline peak near 295 cm^{-1} . With a lower R_H , sample R499 presents a weaker crystalline peak and sample R249 only shows a tiny peak near 290 cm^{-1} . It has been reported that Raman downshifts from 520 cm^{-1} in Si nanocrystals with the decrease in crystal size due to the confinement effects [23,24]. In $\mu\text{c-Ge:H}$ films, the

crystalline peak downshifts from 300cm^{-1} for the same reason [25]. In Fig. 1(b) and (c), TEM shows the details of nanocrystals in sample R999 and sample R499. It is found that the crystal grain density and mean size of sample R499 are smaller than that of sample R999. For the mean size of crystal grains nearly 5 nm, the downshift of Raman $\sim 300\text{ cm}^{-1}$ peak in sample R499 is stronger than that in sample R999.

Fig. 2 shows the deposition rate under different hydrogen dilution ratio. Comparing with the deposition rate at $R_H = 499$, the deposition rate at $R_H = 999$ has a sharp decline, and the initial deposition rate of $R_H = 999$ (0.025 nm/s) is slightly higher than the average rate (0.017 nm/s), for the slope of $R_H = 999$ line reduces at latter half. The deposition rate is 0.07 nm/s for the sample R199, while it is 0.025 nm/s for the sample R999. In PECVD, a low deposition rate can cause great waste of reaction gas. In the manufacturing of semiconductor, at such a low deposition rate (0.017 nm/s, $R_H = 999$), depositing a 100 nm-thickness film needs 2 hours. Therefore, a deposition method, not only promoting the microstructure evolution but also keeping a high deposition rate, is required for manufacture.

3.2 Effect of high plasma discharge power

Plasma energy intensity is one of the key parameters for the deposition of $\mu\text{c-Ge:H}$ films by PECVD [4]. By control of plasma discharge power, ideal plasma energy intensity is achieved. In addition, through discharge power control, quick adjustment of growth process is realized. Fig. 3 and Fig. 4 show two groups of different thickness samples prepared under 5 W and 35 W respectively. Table 2 lists the deposition parameters of these samples. In the process of adjusting time parameters, it is found that crystalline fraction and deposition rate increasing with discharge power increasing. The deposition rate of the 5 W samples closes to 0.015 nm/s, but it is about

0.058 nm/s for the 35 W samples. In addition, in our PECVD system, when the discharge power exceeds 50W, plasma discharge appears unstable phenomenon, thus we chosen a stable condition in the range of 5-35 W.

In Fig. 3(a), Raman scattering spectra shows the microstructure evolution that the crystalline fraction increases with the thickness increasing. The sample P051 and P052 are amorphous, while the sample P053, which crystalline fraction is 31%, is microcrystalline. This demonstrates that the transition from amorphous to microcrystalline phase occurs in 17-29 nm thickness region. Furthermore, it illustrates the thickness of incubation layer is large than 17 nm for this group. In Fig. 3(b-e), the incubation and growth process of crystal grain is investigated by the AFM measurement [26]. In Fig. 3(b) and (c), AFM shows there are some grain structures on the surface of sample P051 and P052, while Raman measurement reflects no crystallization peak of these films. Thus these grain structures are amorphous, or the crystalline volume fraction of these grain structures is too small that the crystalline peak in Raman scattering spectra is covered by amorphous peak. Furthermore, Fig. 3(c), (d) and (e) illustrate the evolution process of the surface morphology from amorphous to microcrystalline. In this process, at first, nucleuses form on the surface of amorphous incubation layer, then it is followed by epitaxial-like growth to develop the crystallite [27]. In addition, according to the nucleation mechanism of $\mu\text{c-Si:H}$ [28], the nucleuses of initial microcrystalline germanium crystal grains should be formed in the region of 17-29 nm.

In Fig. 4(a), Raman measurement shows the crystalline volume fractions of 35 W group, which deposited at a higher discharge power than the 5 W group. The sample P351 has a $X_C = 7\%$ and a thickness of 8 nm, indicating the incubation layer thickness of 35 W samples is less than 8 nm. The thinner incubation layer of 35 W samples indicates that a higher plasma energy density is

benefit to crystal nucleus forming. In addition, with the same thickness, 35 W samples have a higher crystalline fraction than the 5 W samples. Therefore, at high hydrogen dilution conditions, a high energy density further reduces the thickness of incubation layer and increases the crystalline fraction. In Fig. 4(b), (c), (d) and (e), AFM results show the surface morphology of the 35 W samples. Comparing to the 5 W samples, the surface morphology of 35 W samples is rougher and the average grain size is smaller. Especially in the Fig. 4. (e), the sample P354 has a $X_C = 77\%$ and a thickness of 55 nm, however, the average grain size ~ 15 nm obvious smaller than that of sample P054 ~ 40 nm shown in Fig. 3. (e). Although the crystalline fraction of sample P054 only has 67%, the grains are more compact and collision to each other. The sample P354 has smaller grain size than sample P054, but void structures appear between the grains in sample P354.

It was reported that the $\mu\text{-Ge:H}$ with high crystalline fraction tends to consist of compact grains surrounded by more or less open voids [29]. In the plasma process, ion damage is a possible cause of degradation of the film quality, and hydrogen dilution should lead to appearance of microvoid [27]. Furthermore, Matsui et al, reported that Ge dangling bonds at crystalline grain boundaries act as negatively charged acceptors and generate free holes in the films [30]. According to these, if the growth rate of crystal grain is too fast, at the high hydrogen dilution condition, a large amount of void structures will form and the electric properties of films will decrease. In addition, Yan B. et al, reported that though the H_2 dilution profiling technique can partially control the structure homogeneity and improve the $\mu\text{-Si:H}$ solar cell efficiency [13]. Thus, when crystalline fraction increases to a certain degree, it is necessary that holding the growth of crystalline fraction to restrain the defect between crystal boundaries. Moreover, by the

adjustment of the hydrogen dilution and the discharge power, the crystal nucleus formation can be controlled in the $\mu\text{c-Ge:H}$ deposition process.

3.3 Power gradient method

In order to understand the mechanism of the crystal nucleation and the process of microstructure evolution, a group was prepared by the power gradient method at the high hydrogen dilution $R_H = 999$. Table 3 shows the deposition parameters. According to the result of 5 W and 35 W power groups, at 35 W power, crystal nucleuses form faster. When power switches to 5 W, crystals grow along the nucleuses to develop the crystallites. Thus through the power control, we can effectively control the deposition process. At the first stage, we deposited a 3 nm ultrathin film at 35 W discharge power to accelerate the formation of crystal nucleus. And then, we quickly turned down the power to 5 W in a short time (< 5 s) and kept the plasma discharge continue. At 5 W discharge power, the film with crystal nucleuses followed deposition of different time to observe the microstructure evolution. In particular, the deposition rates of the stage 1 and 2 are 0.05 nm/s and 0.015 nm/s, respectively, and close to the deposition rate shown in Table 2.

In Fig. 5(a), Raman scattering spectra shows that all samples are microcrystalline because all samples have the $\sim 300\text{ cm}^{-1}$ peak. First of all, it demonstrates that the crystal nucleuses in the initial 3 nm layer have an intense effect on the amorphous to microcrystalline transition, otherwise the crystalline fractions of this group will approximate to that of the 5 W group. Furthermore, compared with the 35 W and 5 W groups, it is found that the group prepared by power gradient method has a higher crystalline fraction at the same thickness. In Fig. 4(f), the XRD of P345 and G4 indicates the films are microcrystalline, and they have the preferred orientation of 220 [31]. But in the line of sample P353 and G3, there is no obvious crystal peak. It should be the reason that the film is too

thin, and the information of crystal grains cannot be collected effectively. It also means that when the thickness of film less than 30 nm, Raman should be a good method to explore the crystallinity. Fig. 5(d) shows the relationship between crystalline fraction and film thickness. Using the power gradient method, although the discharge power kept at 5 W for most of the deposition time, samples have higher crystalline fraction than that of the 35 W and 5 W samples. In the 5 W group, it is also noticed that, from 17 nm to 29 nm, a region of 12 nm, the crystalline fraction increased from 0 to 31%. Although the deposition rate of 5 W group only has 0.015 nm/s, the crystalline fraction has a quick increase in this region. It means that once the nucleus appears, the crystalline fraction rapidly increases. Therefore, in the power gradient method, crystal nucleuses rapidly form at a high discharge power (35 W), and the evolution from amorphous to microcrystalline is accelerated at a lower discharge power (5 W).

Fig. 5(b) and (c) show the surface morphology of sample G2 and sample G4. It is found that compared with the sample P054 in 5 W group, sample G4 has a smaller average grain size ~20 nm. However, compared with the sample P354 in 35 W group, sample G4 is more compact and has a smaller roughness. This indicates that the nucleuses in the initial 35 W layer of the power gradient method have a significant impact on the following deposition process at 5 W power. In addition, the nucleuses formed at 35 W power even affects the grain size in the 5 W layer. The top layer is deposited at 5 W discharge power, whereas the average grain size closes to the samples of 35 W group. It is attributed to the epitaxial-like growth in the crystal growth [27]. For the crystallites growth along the crystal nucleuses, crystal nucleus also affects the average grain size. Finally, the power gradient method reduces the incubation layer thickness and restrains the crystalline fraction. Thus the formation of crystal nucleuses is a key factor for the initial deposition process of

$\mu\text{-Ge:H}$ thin films.

Fig. 6. (a) shows the TFT structure with a $\mu\text{-Ge:H}$ channel (400 μm width and 200 μm length) and a SiO_2 (270 nm) gate dielectric layer as previously reported elsewhere [32]. Fig.6. (b)(c)(d) show the transfer characteristics of TFTs with $\mu\text{-Ge:H}$ channel layers deposited under different power conditions. All TFTs operate in the linear regime and appear n-type transfer characteristics [32-35]. The mobility μ_e is extracted using the following equation [34]:

$$\mu_e = \frac{1}{C_i V_d} \times \frac{L}{W} \times \frac{\delta I}{\delta V_g}$$

in which I is the drain current, V_g is the gate voltage, L is the channel length, W is the channel width and C_i is the gate insulator capacitance.

At first, the TFT with the power gradient method in Fig.6 (d) has the highest mobility of 0.16 $\text{cm}^2\text{s}^{-1}\text{V}^{-1}$ among the three samples. The mobility of 35 W TFT is 0.099 $\text{cm}^2\text{s}^{-1}\text{V}^{-1}$ while the mobility of 5 W TFT is 0.0056 $\text{cm}^2\text{s}^{-1}\text{V}^{-1}$. With the same device structure and channel layer thickness (20 nm), the different mobility of TFTs should be related to the crystal fraction and the crystal quality of the $\mu\text{-Ge:H}$ channel layer. The channel layer of 5 W TFT is no-crystal material, with a high carrier trapping and recombination rate, which leads to a low carrier mobility. The channel layer of 35 W TFT has higher crystal fraction thus the carrier transport ability is improved. For the power gradient method TFT, the improved performance is not only caused by the higher crystal fraction but also caused by the distribution and size of crystal grain is more homogeneous. Finally, all these results suggest that the quality of $\mu\text{-Ge:H}$ material is controlled by crystal fraction and crystal structure simultaneously.

4. Conclusion

The initial deposition process of $\mu\text{c-Ge:H}$ thin films prepared by PECVD has been studied. The high hydrogen dilution and the high discharge power methods effectively promote the microstructure evolution from amorphous to microcrystalline. In addition, the decrease of deposition rate caused by high hydrogen dilution is compensated by using a higher discharge power, but the rapidly crystal growth leads to smaller average grain size and more void structures in the film. The power gradient method is proposed to understand the mechanism of nucleation and the process of microstructure evolution. It is found that the nucleuses appeared in the initial layer have a great effect on the following deposition process. Especially, the average grain size is at large extent changed for the nucleuses formed at different condition. By the power gradient method, a high crystalline fraction $\mu\text{c-Ge:H}$ film with ultrathin incubation layer ($< 6\text{ nm}$) was deposited at high hydrogen dilution ($R_H = 999$). The forming of crystal nucleuses is promoted at high discharge power, and crystallinity is hold to achieve a homogeneous distribution of the crystal grains at low power. Furthermore, the transfer characteristic of TFT devices shows the power gradient method effectively promotes the electrical properties. As a result, a high quality $\mu\text{c-Ge:H}$ film, 38 nm , $X_C = 48\%$, with an incubation layer less than 6 nm was obtained.

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Table of tables and figures:

Table 1 Deposition parameters and crystalline fractions of $\mu\text{c-Ge:H}$ samples.

Table 2 Deposition parameters of the 5 W, 35 W and 15 W discharge power samples.

Fig. 1. Raman and TEM measurements of $\mu\text{c-Ge:H}$ prepared under different hydrogen dilution ratios. All these samples have a similar thickness about 25 nm. (a) Raman spectra. The signal intensities are normalized to the maximum values. Dashed lines represent the peak of crystalline Ge at 300 cm^{-1} and amorphous Ge at 275 cm^{-1} . (b), (c) TEM images of sample R999 and R499 (5 nm scale). The Ge crystal regions are surrounded by the white dotted circles.

Fig. 2. The relationship between thickness and deposition time. At $R_H = 999$, deposition rate significantly decreases. The inset shows the thickness-time relationship of sample R199, R249, R499 and R999.

Fig. 3. (a) The Raman spectrum of 5 W samples. (b), (c), (d) and (e) AFM images of sample P051, P052, P053 and P054 (1 μm scale).

Fig. 4. (a) The Raman spectrum of 35 W samples. (b), (c), (d) and (e) AFM images of sample P351, P352, P353 and P354 (1 μm scale). (f) X-ray Diffraction of 35w and power gradient samples.

Fig. 5. (a) The Raman spectrum shows the crystal fraction. (b) AFM images of sample G2 with a thickness of 10 nm. (c) AFM images of sample G4 with a thickness of 38 nm. (d) The relationship between thickness and crystalline fraction at high hydrogen dilution $R_H = 999$. The arrow marks show the crystalline fraction increase of the power gradient samples, compared with the 5 W group.

Fig. 6. (a) TFT structure with Ge:H channel layer. (b)(c)(d) I-V transfer characteristic of TFTs

with different deposition power.

Fig. 1. Raman and TEM measurements of $\mu\text{c-Ge:H}$ prepared under different hydrogen dilution ratios. All these samples have a similar thickness about 25 nm. (a) Raman spectra. The signal intensities are normalized to the maximum values. Dashed lines represent the peak of crystalline Ge at 300 cm^{-1} and amorphous Ge at 275 cm^{-1} . (b), (c) TEM images of sample R999 and R499 (5 nm scale). The Ge crystal regions are surrounded by the white dotted circles.

Fig. 2. The relationship between thickness and deposition time. At $R_H = 999$, deposition rate significantly decreases. The inset shows the thickness-time relationship of sample R199, R249, R499 and R999.

Fig. 3. (a) The Raman spectrum of 5 W samples. (b), (c), (d) and (e) AFM images of sample P051, P052, P053 and P054 (1 μm scale).

Fig. 4. (a) The Raman spectrum of 35 W samples. (b), (c), (d) and (e) AFM images of sample P351, P352, P353 and P354 (1 μm scale). (f) X-ray Diffraction of 35w and power gradient samples.

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Fig. 6. (a) TFT structure with Ge:H channel layer. (b)(c)(d) I-V transfer characteristic of TFTs

with different deposition power.

Table 1 Deposition parameters and crystalline fractions of $\mu\text{c-Ge:H}$ samples.

Sample	R_H	Power (w)	Time (min)	Thickness (nm)	X_C (%)
R999	999	15	17	25	34
R499	499	15	13	25	14
R249	249	15	8	25	2
R199	199	15	6	25	0

Table 2 Deposition parameters of the 5 W, 35 W and 15 W discharge power samples.

Sample	R_H	Power (w)	Average deposition rate (nm/s)
P05(1-4)	999	5	0.015
P35(1-4)	999	35	0.058
R999	999	15	0.017

Table 3 Deposition parameters of $\mu\text{c-Ge:H}$ samples.

Stage	Sample	R_H	Power (w)	Total Time (min)	Total Thickness (nm)	X_C (%)
1	G1-4	999	35	1	3	-
2	G1	999	5	5	6	8
	G2	999	5	10	10	15.8
	G3	999	5	20	18	49.5
	G4	999	5	40	38	62.4