Atomic Force Microscopy and Raman Spectroscopy Study of Ge Quantum Dots Growth[a)]

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Abstract

The size and density of the Ge quantum dots by Very Low Pressure Chemical Vapor Deposition have different dependence on substrate temperature compared with the results obtained by MBE. No obvious Si diffusion is found during Ge quantum dots growth at low temperature, but obvious Si diffusion happens when the Ge quantum dots are deposited at high temperature. The existing of hydrogen gas in the reaction chamber may help to take a control of the self-organized growth of the Ge quantum dots or islands on Si substrate.

Introduction

Self-organized growth of semiconductor quantum dots or islands on a different substrate has attracted a great deal of attention because of the capability of tailoring the optical and electronic properties by quantum size effect. The quantum dots or islands grow on a mismatch substrate in Stranski-Krastanov mode under certain conditions. No mismatch dislocations exist in the interface of quantum dots and the substrate. In this case, the size distribution of quantum dots or islands is rather narrow. The most widely studied system is (InGa)As/(AlGa)As for which various quantum effects have already been demonstrated[1,2].

Recently, self-organized growth of Ge quantum dots on Si substrate has been studied[3,4,5,6]. Most of them are fabricated by Molecular Beam Epitaxy (MBE). It's found that the size of Ge quantum dots will increase and the density will decrease as substrate temperature increases[3]. G. Abstreiter etc. also found that the islands or quantum dots were Ge-rich islands and attributed it to Si diffusion from Si substrate to the Ge layer[3]. In this paper, we report the growth of self-organized Ge quantum dots on (100) Si substrate by Very Low Pressure Chemical Vapor Deposition (VLP-CVD) method.

2. Experimental Details

The samples were deposited by Rapid Thermal Process VLPCVD method. The detail of the method has been reported elsewhere[7]. The (100) silicon substrate was standard cleaned before being loaded into the CVD chamber. After general process, 3 sccm of pure SiH_4 flowed to the chamber to deposite Si buffer layer, then 5 sccm of 10% GeH_4 with carrier gas H_2 flowed to deposite Ge film. The growth time of the buffer layer and the Ge film were 1000 s and 300 s, respectively. The growth substrate temperature was changed from 600 to 750. The growth pressure was of the order of 0.1 Pa.

The samples were analyzed by Raman scattering and Atomic force microscopy (AFM). The Raman spectra of the samples were recorded at room temperature on SPEX Raman spectrometer in a quasibackscattering geometry using 300 mW of argon laser light at 488 nm for excitation. The wavenumber resolution was 0.5 cm^{-1}. The standard Si sample was used to calibrate the wavenumber of monochromator. Surface morphologys of the samples were measured by tapping mode atomic force microscopy in air.

3. Results and Discussion

VLPCVD is surface-controlled reaction, which including germane adsorption on growing surface and hydrogen desorption from

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it. The growth rate then depends on substrate temperature[8]. At low temperature, hydrogen desorption rate is low, so the surface is mostly covered with hydrogen atoms. Therefore, the growth rate is controlled by hydrogen desorption and increases a lot as the temperature increases. However, at high temperature, hydrogen desorption rate is high, then the hydrogen coverage of the surface is low. Thus germane adorption is the controlling factor of the growth procedure. the growth rate increases a little as the temperature increases accordingly.

During sample growth by RTP/VLP-CVD, substrate temperature is high enough for hydrogen to desorb from growing surface. So germane adsorption may be the controlling factor of growth at such high temperature. However, the carrier gas hydrogen in the chamber will reduce hydrogen desorption rate from the growing surface. In this case, proper hydrogen coverage on the surface may be possible, then hydrogen desorption from the surface may be the controlling factor of growth even at rather high temperature.

The hydrogen coverage and the growth rate were obtained from the following equations:

$$r = P_1/RT \{K_1 \sigma^2\} \qquad (1)$$

$$r' = \beta \sigma_H \qquad (2)$$

Where, P is the partial pressures of GeH_4. σ and σ_H are the surface coverage of Ge and GeH_4 respectively. K is the adsorption constants of GeH_4 on Ge vacancy sites respectively. β is the desorption constant of hydrogen from GeH_4 site. r is adsorption rate decided by GeH_4 adsorption on growing surface. r' is desorption rate decided by hydrogen desorption from GeH site. The detail of the equations can be found elsewhere[9]. In our calculation, we have assumed that one hydrogen molecule adsorbing on Ge sites can produce two GeH sites.

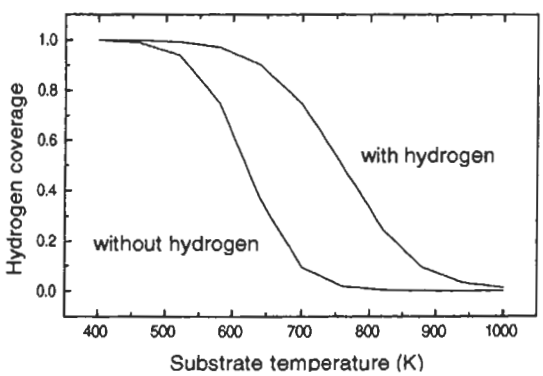


Fig.1 The calculation results of hydrogen coverage on growing surface versus the substrate temperature with and without hydrogen.

Fig.1 is the calculation results of hydrogen surface coverage on growing surface versus the substrate temperature. In this calculation, the germane adsorption and the desorption constants are sited from Reference[9]. The hydrogen adsorption constants is based on the assumption that the adsorption active energy of hydrogen on Ge surface is the same as that of the germane. The coefficient of hydrogen adsorption constant is sited from Reference[10], and we have neglected the influence of the substrate. This figure shows that the hydrogen coverage has increased a lot since the hydrogen gas is added to the reaction gases.

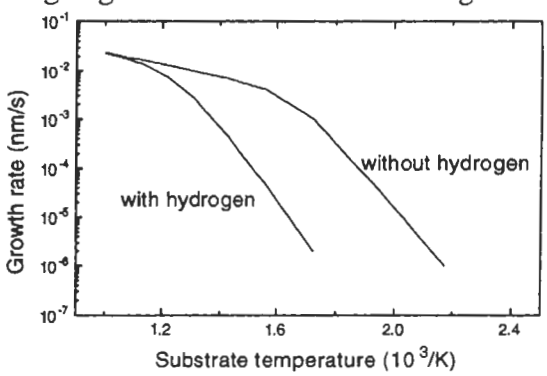
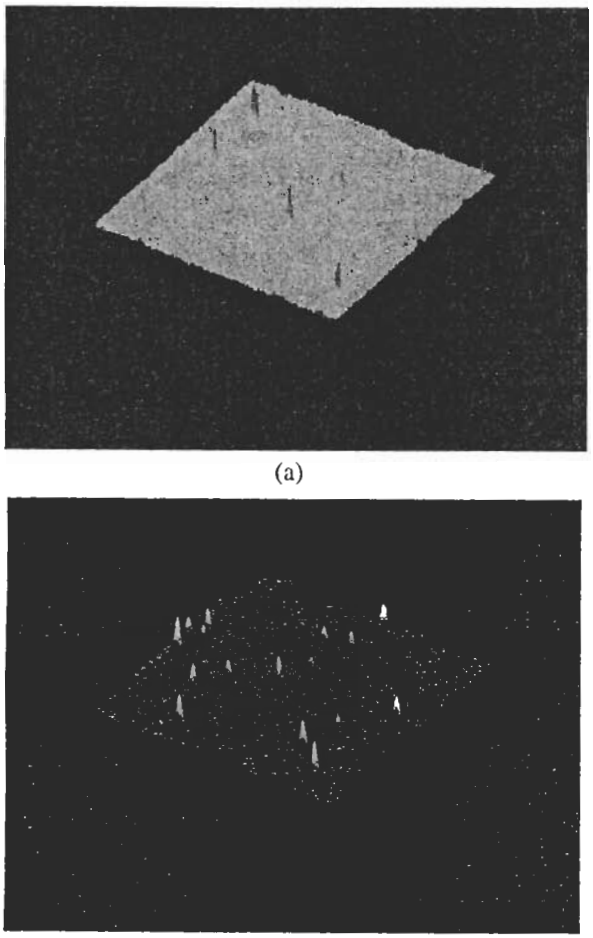


Fig.2 The calculation results of the growth rate versus the substrate temperature with and without hydrogen.

Fig.2 is the calculation results of the growth rate with and without hydrogen. This figure shows that the growth rate decreases a lot when hydrogen gas is added into chamber. So even at the high temperature (about 600), the hydrogen coverage on the growing surface also exists and the growth is then controlled by hydrogen desorption process. As the temperature increases, the growth controlling factor may be changed from hydrogen desorption to germane adsorption. However, in MBE, the growth is always controlled by the adsorption of reaction atoms. Therefore, the growth rate does not vary with the temperature.

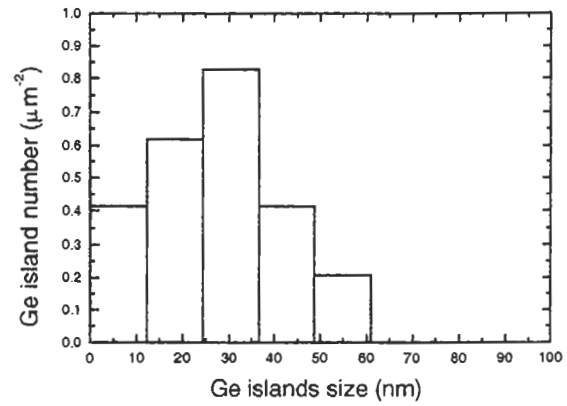
Mentioned above shows the growth procedure of CVD is different from that of MBE. So compared with the results obtained by MBE, Ge quantum dots or islands growth by CVD may have a different dependence on substrate temperature. Fig.3 is the AFM images of Ge quantum dots or islands deposited at different



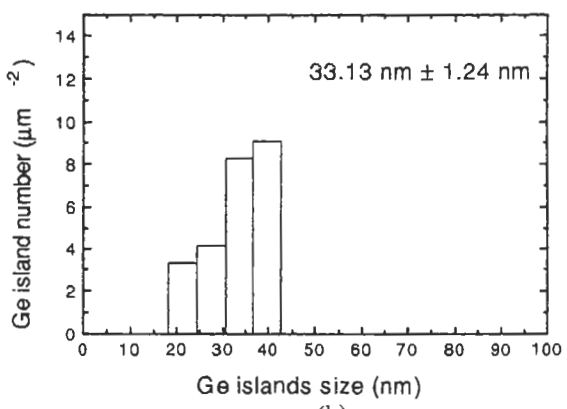
(a)

(b)

Fig.3 The AFM images of the Ge quantum dots or islands deposited at different temperatures (a: 600℃, b: 650℃).



(a)



(b)

Fig.4 The number of quantum dots (islands) number versus island sizes (a: 600℃, b: 650℃).

temperatures (a: 600, b: 650). From the plane images (not shown here) of Fig.3, Fig.4 shows the quantum dots (islands) density versus quantum dots (islands) size. It is obviously that the density of Ge quantum dots (or islands) increases and the size distribution becomes narrow as substrate temperature increases. This result is different from that obtained by MBE method[3], where the density decreases and the size increases as substrate temperature enhance.

This phenomenon can be explained as follows. At low temperature, hydrogen coverage on growing surface is high. This will reduce Ge atom migration ability, so the Ge atoms adsorbing near a large quantum dot cannot migrate to a small quantum dot even under the strain related effect[11]. Thus the size distribution will be large. As temperature increases, the situation will change. On one hand, hydrogen desorption rate will increase, and the hydrogen coverage of the surface will reduce. Therefore, high density of vacancy sites in the surface will lead the density of nucleated centers to increase and as well as the density of quantum dots. On the other hand, low hydrogen coverage of the growing surface by high temperature will enhance Ge atom migration ability. Consequently, the Ge atoms adsorbing near a large quantum dot can migrate to a small quantum dot due to the strain related effect[11]. So the size distribution will be rather narrow.

As shown in Fig.2, the growth rate will increase much as substrate temperature increases at low temperature regime9. So, similar to the results obtained in MBE, the density of the quantum dots will increase as the temperature increases[3]. This shows that the high growth rate at high temperature may also influence the quantum dots growth just like the influence of low hydrogen coverage by high temperature. No matter which influences more, the above results show that the growth temperatures of Sample a and b are at low temperature regime of the VLPCVD reaction.

As the temperature increases to 700 (Sample c), both the density and size of the quantum

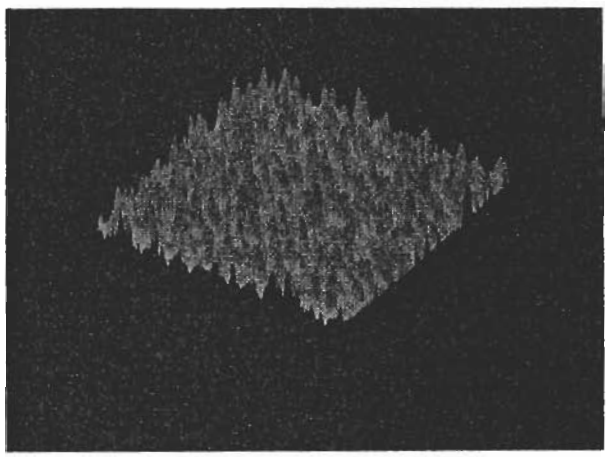


Fig.5 The AFM image of the sample c deposited at 700℃.

dots increase. Fig.5 is the AFM image of the sample deposited at 700. The high density of the quantum dots is also because of lower hydrogen coverage and higher growth rate by high temperature. However, the larger size is due to the high Ge coverage by high growth rate.

Fig.6 shows the Raman Scattering spectra of Sample a and b. From this figure, we can find that Si-Ge vibration mode nearly 400 cm^{-1} is very weak compared with the noise, and the intensity increases a little as temperature increases. The Ge-Ge vibration mode nearly 300 cm^{-1} is pronounced. So we can say that Si diffusion from Si substrate to the Ge film is small. This result is different from that obtained by MBE[3], where Ge film is found to be Ge-rich islands by Si diffusion from Si substrate. The reason may be because proper hydrogen coverage on growing surface at low temperature will also decrease the Si diffusion rate from Si substrate. The existing Ge-Si weak peak may come from the Ge wetting layer. Because a fraction of the Si and Ge atoms in the outmost two layers of the growth front can exchange.

High temperature will increase Si diffusion rate from Si substrate. Fig.7 shows the Raman Scattering spectrum of Sample d, which is deposited at the temperature of 750. Different to the samples deposited at low temperatures, obvious Ge-Si vibration mode is found nearly 400 cm^{-1} . We ascribe this to be Si diffusion from Si substrate at an enhanced rate by high temperature and lower hydrogen coverage. The AFM image of Sample d (not shown here) shows that the size of Ge islands becomes large and the density decreases compared with sample c. This result is accord with that obtained in MBE[3]. We believe at such high temperature, just like the calculation results in Fig.1 and 2, hydrogen desorption rate is high enough, and then the hydrogen coverage is very small. The growth temperature of sample d is then at high temperature regime. So the growth is controlled by germane adsorption on the surface, and the growth rate varies a little with the temperature. This growth situation is similar to that of MBE. It is not strange to observe this similar phenomenon of Ge quantum dots growth at such high temperature.

4. Conclusion

In summary, Ge quantum dots growth by VLPCVD has a different dependence on substrate temperature compared with that

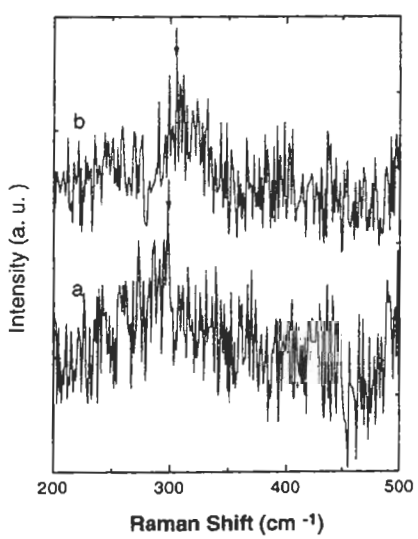


Fig.6 The Raman Scattering spectra of Sample a and b (a: 600℃, b: 650℃).

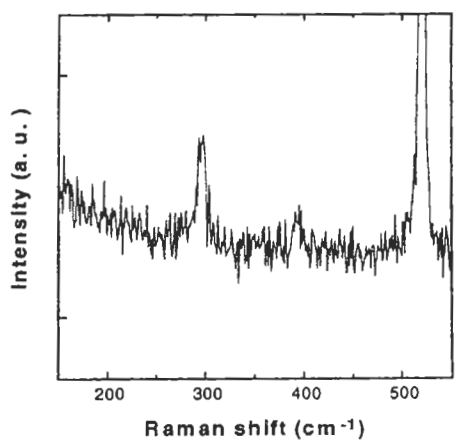


Fig.7 The Raman Scattering spectra of Sample d deposited at 750℃.

obtained by MBE. This is attributed to the influences of surface-controlled reaction and proper hydrogen coverage on growing surface. No obvious Si diffusion is found during Ge quantum dots growth at low temperature, but obvious Si diffusion happens when the Ge quantum dots are deposited at high temperature. Proper hydrogen coverage on the growing surface may be useful to control the self-organized growth of Ge quantum dots or islands on Si substrate. Proper substrate temperature is also important to deposite Ge quantum dots with high density and narrow size distribution by the VLPCVD method.

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