

Investigation of the size effect on optical properties of polycrystalline Ge deposition by pulse laser deposition

XIYING MA, WEILIN SHI

Institute of Optoelectronic Materials, Department of Physics, Shaoxing College of Arts and Sciences, Shaoxing, 312000, Zhejiang Province, People's Republic of China
E-mail: xiyingma@sohu.com

Published online: 4 February 2006

The size effect of optical properties of the polycrystalline Ge/Si films prepared by pulse laser deposition (PLD) is investigated by photoluminescence (PL) and photocurrent (PC) spectra. The size of Ge nanocrystals is precisely controlled by the pulsed deposition time and then observed by the atomic force microscopy (AFM). The average size of Ge nanocrystals is about 2, 5 and 25 nm for 1, 2 and 3 min deposited sample, respectively. The size effect on optical properties of Ge nanocrystals has been analyzed by photoluminescence (PL) and photocurrent (PC) spectra. The PL peaks shift from 0.799 eV for 1 min to 0.762 eV for 3 mins; at the same time, the photocurrent peaks of the films sharply changes from 0.781 eV to 0.749 eV, the shifts of PL and PC are contributed to the quantum size effect of Ge nanocrystals.

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1. Introduction

The advances in growth techniques have led to improving optical quality of Ge/Si heterostructures, which allow the design of photo-electronic devices [1, 2]. Band-gap engineering of indirect-to-direct conversion structures using Si/SiGe material system attracts considerable interest [3, 4]. Recently, the reports on the optical properties of porous-Si suggest that this conversion may result in the formation of quantum confinement structures [5, 6]. There are many contributions on Ge quantum dot deposited by MBE [7, 8], low-pressure chemical vapor deposition and other methods [9]. However, the studies on Ge nanocrystals growth by pulsed laser deposition (PLD) are not often seen [10–12]. As one of the most convenient technique, PLD is often used to prepare various nanocrystal thin films because the size of nanocrystals can be precisely controlled by the laser pulsed time [13, 14].

In the present study, we deposited Ge polycrystalline films by PLD method, the size of the Ge nanocrystals is precisely controlled by the pulsed deposition time and then observed by the atomic force microscopy (AFM). The optical properties and the quantum size effect have been studied by the photoluminescence (PL) and the photocurrent spectra. The energy shifts of PL and PC peaks in the spectra agree with the calculated quantum confinement effect.

2. Experiment

The polycrystalline nanometer Ge thin films were fabricated by pulsed laser deposition on p-Si (100) substrate at room temperature. A Lambda Physik LPX 305 KrF ($\lambda = 248$ nm) excimer laser with an energy density of 0.75 J/cm^2 and with a pulse duration of 25 ns was employed as the irradiation source. The laser beam is a near Gaussian profile and incident on the sample at an angle of 45° . The beam was focused with three pieces of lens so as to produce a laser spot of 0.8 mm in diameter on the surface. The laser beam was introduced into the deposition chamber through a ultra-violet window. The Ge target was placed at the focus position of the lens. The p-Si (100) substrate used in the study were cleaned and degreased with acetone and methanol. After rinsing in de-ionized water, they were subjected to etch by the $\text{H}_2\text{O}:\text{HF} = 10:1$ solution for one minute in order to remove the oxides. Finally, they were dried by blowing N_2 gas and put into the deposition chamber. The working pressure was in a range of 50 Pa during deposition. The distance between the substrate and the Ge target is 8 cm. The microscopy of the Ge polycrystalline deposited at 1, 2 and 3 min and then the deposited thin films were rapidly annealed *in situ* in the atmosphere of Ar gas at temperature of 500°C and pressure of 500 Pa for 5 min, and then cooled down to room temperature.

The samples were investigated by AFM in tapping mode at room temperature. The photoluminescence of the annealed samples were excited by a 514 nm Ar⁺ laser line with an excitation power of 30 mW and the beam was focused to a sample area of approximately 2 mm² at 300 K. The photocurrent was measured on a 200 μm diameter mesa of the sample working as a photodetector. A light radiated from a tungsten lamp with an intensity of 40 mW · cm⁻² through a monochromator spectrometer and two lens normally focusing on the samples at 300 K.

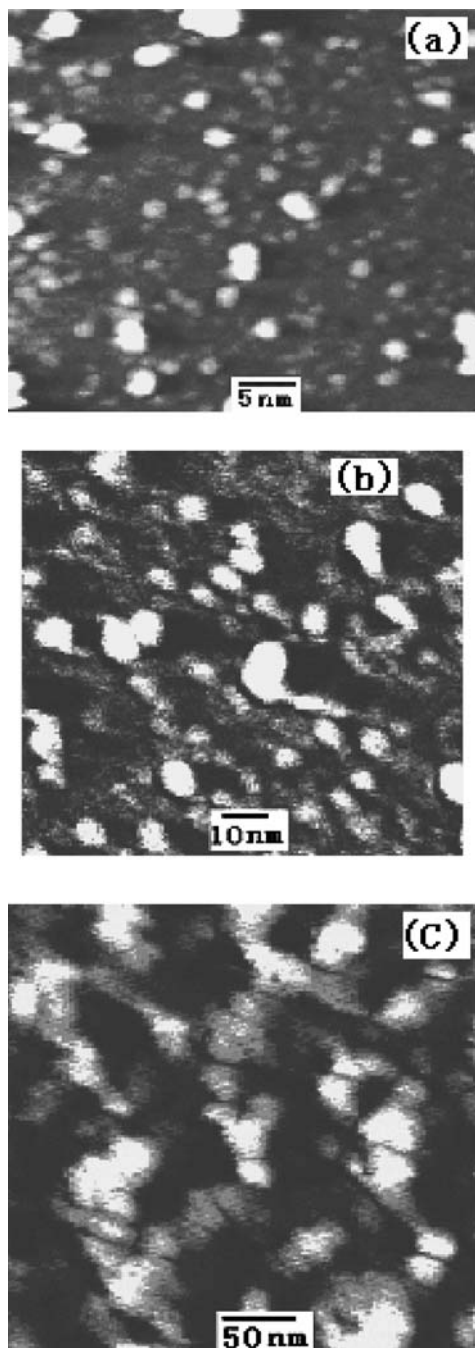


Figure 1 The AFM images of Ge nanocrystal sample deposited for (a) 1 min, (b) 2 mins and (c) 3 mins. The films are composed of polycrystalline Ge.

The photocurrent signal was detected by a lock in amplifier with a band of 5 Hz to suppress the dark current at the reverse voltage bias 10 V. And the measured data was digitally converted and processed by a computer.

3. Result and discussion

Fig. 1a, b and c show the AFM images of polycrystalline nanometer Ge films deposited for 1, 2 and 3 min and then annealed at 500°C for 5 mins, respectively. For 1 min deposition time, it is not formed the continuous film and this process can be considered as a nucleation stage, the monodispersed Ge nanoparticles about 2 nm are scattered on the substrate surface. The particles in Fig. 1b link each other and the size of them is about 5 nm. Fig. 1c is consisted of Ge clusters with the average size of 25 nm. Clearly, the size of the Ge nanocrystals becomes larger with the increasing growth time. That is to say, under the same other conditions, the size of Ge nanometers can be controlled by the pulsed deposition time. On the other hand, the size of the Ge grains is getting more and more homogeneous with growth time that is accordance with the tendency of films formation.

Fig. 2 shows the photoluminescence (PL) spectra of above samples. Among the four spectra, the largest PL intensity is from the 1 min sample. The peaks of 1, 2 and 3 samples are located at 0.799, 0.787 and 0.762 eV, respectively, which are contributed by the direct transition from conductor band to the valence band of Ge nanocrystals. The PL band becomes very board due to the large size distribution of Ge with increased deposition time. The PL spectrum of 5 mins is a no-structured wide band featuring the optical properties of large cluster, which is similar to that of bulk Ge. In addition, with the increasing growth time, the PL intensity of the spectra become weak, and the peaks shift to lower photo energy, these results can be interpreted in terms of the quantum size effect.

Since Ge is an indirect semiconductor, the quantum efficiency of light emission is very low because the production of photons is achieved by the assistance of phonon for

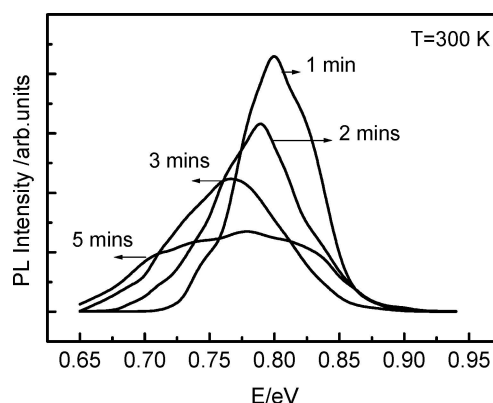


Figure 2 The PL spectra of deposited for 1, 2 and 3 and 5 mins. With the increasing growth time, the PL peaks of the spectra shift to lower photo energy.

momentum conservation. Moreover, this luminescence is quenching at room temperature. However, the polycrystalline of Ge is a typical fractal-like microstructure; the disorder factor plays a key role in the luminescence of Ge nanocrystals. Size distribution and quantum size effect give rise to the distribution of potential barriers. Therefore, the processes of tunneling and migration of electrons and excitations become possible. The observed PL signals in Ge nanocrystals films result from the increasing probability of electrons and holes combination while bulk Ge quenching at room temperature.

The energy shifts of PL and PC peaks with the size of Ge particles relevant to the quantum confinement effect in Ge nanocrystals. The confinement effect can be estimated according to Kayanuma equation, which is a more precise relationship between particle size and energy by taking the finite barrier height into account [15].

$$E_{1s1s} = E_g + \pi^2 \frac{a_B}{a} Ry^* - 1.786 \frac{a_B}{a} Ry^* - 0.248 Ry^* \quad (1)$$

where E_{1s1s} denotes the ground state energy level of Ge nanocrystals; E_g is the energy band gap of bulk Ge (0.66 eV), a_B , Ry^* and a is the exciton Bohr radius, Rydberg energy and the radius of Ge nanocrystals, respectively. In Equation (1), the second term describes the absorption edge shift due to quantum confinement effect, and the third term denotes the Coulomb interaction of the electron-hole pair. According to the like-hydrogen model,

$$a_B = \epsilon \frac{m_0}{\mu} a_0, \quad Ry^* = \frac{e^2}{2\epsilon a_B}, \quad (2)$$

$a_0 = 0.53 \text{ \AA}$, $a_B \approx 18.4 \text{ nm}$ and $Ry^* = 2.5 \text{ meV}$ for bulk Ge [16].

The energy difference due to the quantum confinement effect with respect to bulk Ge can be written as

$$\Delta E = E_{1s1s} - E_g \quad (3)$$

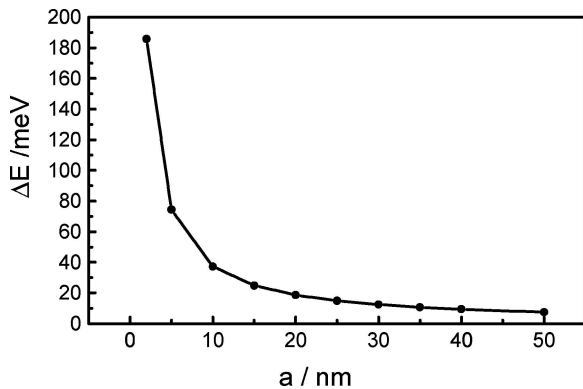


Figure 3 The energy dependence of the size of Ge nanocrystals. The quantum confinement effects become smaller with increasing growth time.

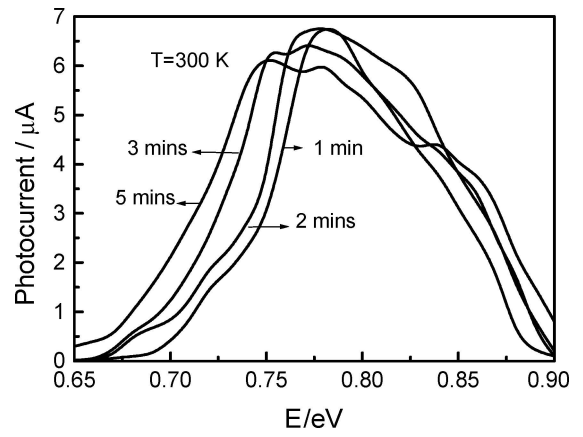


Figure 4 The photocurrent spectra of the samples deposited for 1, 2, 3 and 5 mins. The photocurrent responsivity range becomes broader with growth time.

The radius of Ge nanocrystals is estimated from Fig. 1a, b and c as $a_1 = 2 \text{ nm}$, $a_2 = 5 \text{ nm}$ and $a_3 = 25 \text{ nm}$, respectively. Inserting them into Equations 1 and 3, the energy difference ΔE is 185.07, 73.6 and 36.52 meV, respectively. It indicates that the smaller the size, the stronger the quantum size effect is. The energy difference ΔE dependence of the size of Ge nanocrystals is shown in Fig. 3, with increasing deposition time, the energy difference become smaller and smaller, and the behave tendencies to that of bulk Ge.

Inversely, Combining the energy difference ΔE values 185.07, 73.6 and 36.52 meV with the energy band gap 0.66 eV of bulk Ge, the PL peaks of 1, 2 and 3 mins samples in Fig. 2 should located at 0.845, 0.734 and 0.732 eV. However, in fact, the PL peaks of 1, 2 and 3 mins are located at 0.799, 0.787 and 0.762 eV in Fig. 2, respectively. There is a little difference between them, which can be interpreted in terms of the size distribution of Ge nanocrystals. For example, $\Delta E = 185.07$ at the average size of $a_1 = 2 \text{ nm}$ for Fig. 1a is not precise due to there is a size distribution. There is another PL curve for deposited 5 mins, we can see the spectrum is very broad that similar to the optical feature of bulk Ge.

Fig. 4 shows the photocurrent spectra of 1, 2, 3 and 5 mins samples. The energy peak of 1 min sample is located at 0.781 eV, and the corresponding wavelength is 1.58 \mu m ; and the energy peak of 3 mins is located at 0.749 eV, the wavelength is 1.65 \mu m . That indicates the cut off wavelength extends to longer wavelength with deposition time, at the same time, the responsivity range become wider due to the size distribution in the films, and the peaks of the spectra have a little shift towards lower photon energy for the quantum size effect.

4. Conclusions

The growth and optical properties of the Ge nanocrystals deposited by PLD have been studied using AFM and photoluminescence (PL) spectra. The size of the Ge crystals can be controlled by the pulsed deposition time. The PL peaks shifts from 0.799 eV of 1 min to 0.762 eV of

3 mins indicating that the PL energy strongly depends on the size of Ge nanometer due to the quantum size effect, at the same time, the photocurrent spectra (PC) of the films sharply changes from 0.781 eV to 0.749 eV.

Acknowledgement

This work was supported by the National Natural Science Foundation (Grant No. 60276025) and the Postdoctor Foundation of Lanzhou Institute of Physics, Chinese Academy of Space and Technology.

References

1. S. S. IYER and Y. H. XIE, *Science* **260** (1993) 40.
2. U. MIESNER, K. BRUNNER and G. ABSTREITER, *Thin Solid Films* **380** (2000) 180.
3. U. GNUTZMANN and K. CLAUSECKER, *Appl. Phys.* **3** (1974) 9.
4. K. DETTMER and J. WEBER, *Thin Solid Films* **222** (1992) 234.
5. L. T. CANHAM, *Appl. Phys. Lett.* **57** (1990) 1046.
6. S. GARDELIS, J. S. RIMMER, P. DAWSON and B. HAMILTON, *ibid.* **59** (1991) 2118.
7. C. MIESNER, O. R. OTHIG, K. BRUNNER and G. ABSTREITER, *Physica E* **7** (2000) 146.
8. G. MEDEIROS-RIBEIRO, D. LEONARD and P. M. PETROFF, *Appl. Phys. Lett.* **66** (1995) 1767.
9. F. BOSCHERINI, G. CAPELLINI, L. DI GASPARE, M. DE SETA, F. ROSEI, A. SGARLATA, N. MOTTA and S. MOBILIO, *Thin Solid Films* **380** (2000) 173.
10. S. TAKEOKA, M. FUJII, S. HAYASHI and K. YAMAMOTO, *Phys. Rev. B* **58** (1998) 7921.
11. K. M. HASSAN, *et al.*, *Appl. Phys. Lett.* **75** (1999) 1222.
12. E. HARO-PONIATOWSKI, R. SERNA, A. SU'AREZ-GARCIA, C.N. AFONSO, M. JOUANNE and J. F. MORHANGE, *Appl. Phys. A* **79** (2004) 1299.
13. M. S. ZHANG, P. ZHANG, Z. YON and J. LIN, *ibid.* **69** (1999) 389.
14. F. VROEGINDEWEIJ, E. A. SPEETS, J. A. J. STEEN, J. BRUGGER and D. H. A. BLANK, *ibid.* **79** (2004) 743.
15. Y. KAYANUMA and H. MOMIJI, *Phys. Rev. B* **41** (1990) 10261.
16. H. TEMKIN, T. P. PEARSALL and J. C. BEAN, *Appl. Phys. Lett.* **48** (1986) 963.

*Received 15 January
and accepted 5 May 2005*