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# Fabrication of luminescent ge nanocrystals started from unlayered hydrogenated amorphous SiGe films or hydrogenated amorphous Si/hydrogenated amorphous Ge multilayers

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**Abstract.** Nanocrystalline Ge embedded in $SiO_x$ matrix is fabricated by oxidizing hydrogenated amorphous SiGe alloys or hydrogenated amorphous Si/hydrogenated amorphous Ge multilayers. The structures before and after oxidation are systematically investigated. Visible light emission was observed from both samples. The luminescence peak is located at 2.2 eV which is independent of the starting materials. Compared to the luminescence from unlayered samples, the photoluminescence spectrum from multilayered samples has a narrower band width, which can be attributed to the uniform size distribution. The light emission origin is also discussed briefly and a mechanism different from the quantum size effect is suggested.

## 1. Introduction

The study of group-IV semiconductor nanocrystals embedded in solid matrices is currently attracting much interest because they are expected to show different optical and electric properties from their bulk counterparts [1, 2]. Particularly, an intense visible light emission could be realized at room temperature from nanocrystalline Si (nc-Si) and nanocrystalline Ge (nc-Ge) films, though the origin is still unclear [3, 4]. The quantum size effect is generally thought to play an important role in the visible light emission process in these nanocrystalline materials [3, 5]; however, discrepancies with the quantum confinement model have been reported by several groups [4, 6]. The reason may be the broad size distribution of nanocrystalline semiconductors and the influence of surface states [7].

The system of nc-Ge embedded in $SiO_2$ host matrix is one of the promising candidates to be studied since Ge has smaller electron and hole effective mass and larger dielectric constant compared with Si, which results in a larger Bohr radius [4]. Moreover, $SiO_2$ layers can passivate nc-Ge very well to reduce the surface states. Thus, the size-dependent properties should be much easier to observe in nc-Ge materials. So far, many approaches have been proposed to fabricate the nanocrystalline Ge, such as the epitaxial growth of SiGe alloys with subsequent dry or steam oxidation [8]. Co-sputtering of Ge and $SiO_2$ with subsequent annealing [9] and direct preparation by the CVD technique [10]. It has been reported that, with annealing the SiGeO alloys at high temperature, Ge element can be precipitated to form Ge clusters with nanometre size, while oxygen was bonded to Si to form an $SiO_2$ matrix [4].

It was also reported that hydrogen can be helpful for the formation of small Ge clusters in this system [11]. In this paper, we firstly prepare nc-Ge embedded in Si oxide matrices simply by oxidizing hydrogenated amorphous silicon–germanium (a-SiGe:H) alloys. The structures of samples before and after oxidation treatment were systematically investigated as a function of oxidation time. A broad and visible light emission has been observed at room temperature. Based on the above results, we then attempt to obtain the nc-Ge by oxidizing hydrogenated amorphous Si/hydrogenated amorphous Ge (a-Si:H/a-Ge:H) multilayers, since multilayered structures have many advantages in controlling the size distribution of nanocrystals and in future actual applications [3, 12]. An intense visible photoluminescence with narrow bandwidth has also been observed and the PL peak energy is almost the same as that started from unlayered films.

## 2. Sample preparation

Both unlayered a-SiGe:H alloys and layered a-Si:H/a-Ge:H multilayers were deposited in a capacitively coupled plasma enhanced chemical vapour deposition (PECVD) system excited by using 13.56 MHz radio frequency power. During the deposition, the substrate temperature is 200 °C and the rf power is 20 W. Gas mixtures of $GeH_4$, $SiH_4$ and Ar were introduced into the deposition chamber and their flow rate can be carefully controlled by a mass flow meter (MKS 260). For a-SiGe:H film deposition, the $SiH_4$ flow rate is changed from 2 to 5 sccm and the $GeH_4$ flow rate is kept at 1 sccm. The total thickness is around 300 nm. For a-Si:H/a-Ge:H multilayer deposition, both a-Si:H and a-Ge:H sublayer thicknesses are designed as 3 nm and the total thickness of layered samples is about 200 nm. The $SiH_4$ and $GeH_4$ flow rate is controlled at 5 and 1 sccm, respectively. c-Si(100) wafers and Corning 7059 glass plates were used as substrates for different measurements.

Oxidation was carried out in a conventional tube furnace at the oxidation temperature of 800 °C. The dry–wet–dry oxidation process was used, in which the dry oxidation time is kept at 10 min and the wet oxidation time was changed from 10 to 70 min (hereafter, the oxidation time only refers to wet oxidation time).

The samples before and after oxidation were characterized by using Fourier transform infrared (FT-IR) spectroscopy, Raman scattering and x-ray diffraction (XRD) techniques. Raman scattering measurements were carried out at room temperature by using an $Ar^+$ laser (488 nm) as an excitation light. The Cu K$\alpha$ line was used as x-ray source in XRD experiments. The microstructures of oxidized samples were also investigated by the electron diffraction pattern. Photoluminescence (PL) was measured in a SPEX system at room temperature by using the $Ar^+$ laser as excitation light.

## 3. Results and discussion

### 3.1. Unlayered a-SiGe:H alloys

Figure 1 shows the typical FT-IR spectrum for unlayered a-SiGe:H alloys with and without oxidation treatment. In the spectrum of as-deposited samples, the wagging mode of Si–H (630 cm$^{-1}$), Ge–H (570 cm$^{-1}$), and stretching mode of Ge–H and Ge–H$_2$ (1875–2000 cm$^{-1}$), Si–H and Si–H$_2$ (2000–2100 cm$^{-1}$) can be clearly identified in the spectra. The vibration peaks around 700–900 cm$^{-1}$ can be attributed to the presence of the Si–H$_2$ and Ge–H$_2$ band. After oxidation at 800 °C, all the vibration modes related to the hydrogen disappeared and a strong Si–O band (around 1100 cm$^{-1}$) appeared obviously in the spectrum. It is worth noting that the Ge–O band (around 900 cm$^{-1}$) cannot be observed in the present FT-IR spectra, which
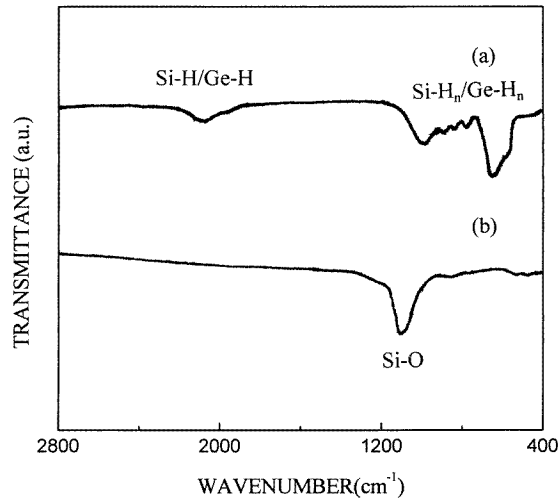
**Figure 1.** FT-IR spectrum for (a) as-deposited a-SiGe:H film and (b) a-SiGe:H films after oxidizing at 800 °C for 2 h.
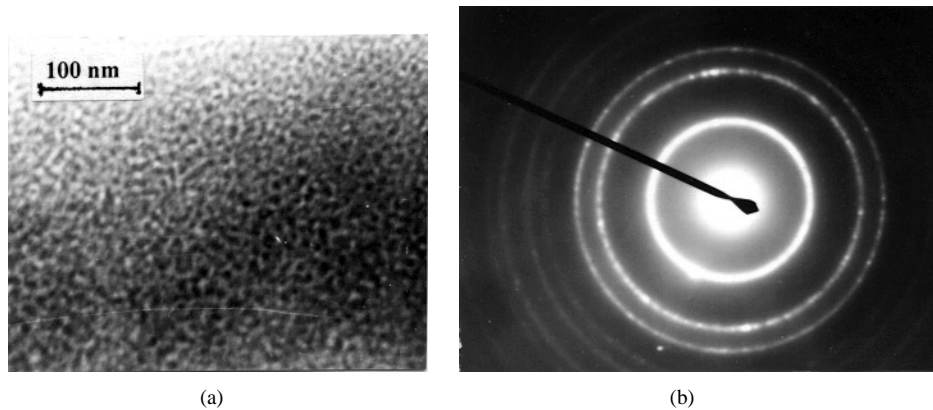


**Figure 2.** (a) Cross section TEM photograph of oxidized a-SiGe:H films. (b) ED pattern for the same sample.

implies that during the oxidation in our examination range, only Si atoms in the alloys were oxidized and Ge is remained in the films as a Ge–Ge form.

The cross section transmission electron microscopy (TEM) image of oxidized a-SiGe:H film is shown in figure 2(a) and the electron diffraction (ED) pattern is given in figure 2(b). From the TEM image, the precipitated particles, whose size is less than 10 nm, can be observed. The results calculated from ED pattern are 3.27, 1.96, 1.68 and 1.39 Å, respectively, which correspond to the Ge(111), (220), (311) and (400) planes. It is indicated that, during the oxidation, Ge was precipitated and Ge clusters with the size of several nanometres were formed. Figure 3 is the Raman spectra for a-SiGe:H alloys oxidized at 800 °C for different wet oxidation time. It is found that the Ge–Ge TO mode ($\sim 300$ cm$^{-1}$) and Si–Ge TO mode ($\sim 390$ cm$^{-1}$) can be observed when the wet oxidation time is less than 30 min. The Ge–Ge vibration peak becomes sharper and more intense with increasing the oxidation time from 10 to 30 min, then the peak becomes broader and weaker with further oxidation. The Si–Ge signals cannot be detected and the Si–Si TO vibration mode can be observed after 50 min wet
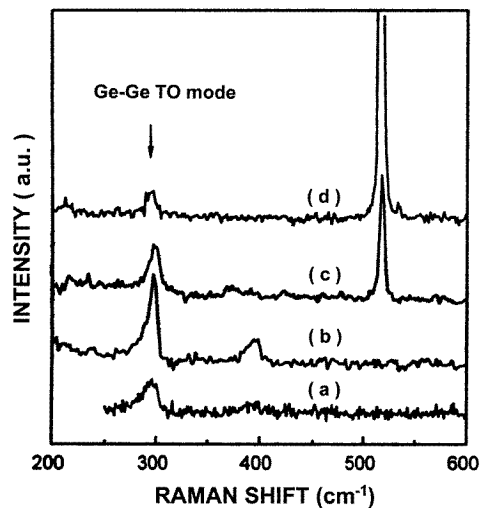
**Figure 3.** Raman spectra for a-SiGe:H films oxidized at 800 °C for different wet oxidation time.
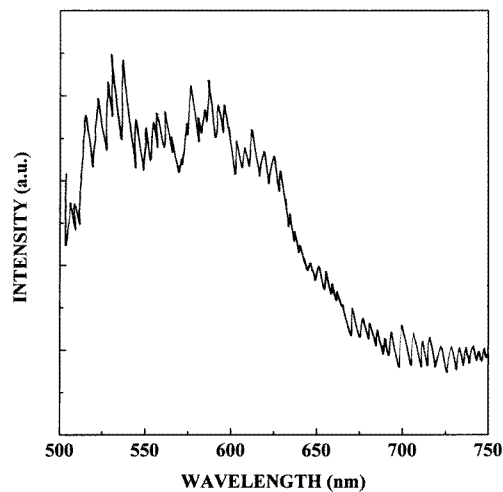


**Figure 4.** Room temperature photoluminescence spectrum for unlayered a-SiGe:H film oxidized at 800 °C for 70 min.

oxidation. The average size of Ge clusters can be estimated from the shape and full width at half maximum (FWHM) of the Ge–Ge TO peak from Raman spectra [9]. After 30 min wet oxidation, the size of Ge clusters is about 8.6 nm. The size decreases to 5 nm with further oxidation.

According to Kanemitsu's results, at the relatively low temperature of 800 °C, the nucleus radius of Ge is as small as 1 nm. Also, considering that the free energy of $SiO_2$ and $GeO_2$ formation is quite different at 800 °C, (for $SiO_2$ −765.45 kcal mol$^{-1}$ and for $GeO_2$ −424.43 kcal mol$^{-1}$) [13], oxygen will selectively bond to Si atoms and small Ge clusters can be simultaneously formed. Due to this selective oxidation process in a-SiGe:H films, Si is firstly oxidized and Ge can be precipitated to form small clusters in the nanometre scale, which will aggregate to form Ge clusters with increasing oxidation time at 800 °C. When all

the Si has been oxidized the oxidation of Ge can occur to form $GeO_x$ and the formed nc-Ge is surrounded by $SiO_x$ matrix. Thus, the Ge-related vibration modes can be observed in Raman spectra and the Si–Si signals cannot be found when the oxidation time is less than 30 min. Further oxidation will induce the oxidation of Ge clusters which results in the Ge–Ge vibration peak becoming broader and weaker and the size of nc-Ge decreases. The Si–Si signals from c-Si substrate can be detected as shown in figure 3(c) and (d) since the sample becomes more transparent after oxidation.

A typical room temperature photoluminescence spectrum for unlayered a-SiGe:H film oxidized at 800 °C for 70 min is given in figure 4. It is worth pointing out that room temperature light emission cannot be observed from as-deposited samples. After oxidation, a weak luminescent signal can be detected. As shown in figure 4, the PL peak is located at 2.2 eV, which is in the orange–green range, and the FWHM of the PL peak is about 0.54 eV. It seems that the PL peak is almost unchanged with oxidation time and the PL intensity is varied with increasing oxidation time.

### 3.2. a-Si:H/a-Ge:H multilayers

In order to further study the photoluminescence characteristics from the nc-Ge/$SiO_x$ system, a new approach, that of oxidizing the starting material of a-Si:H/a-Ge:H multilayers to obtain nc-Ge/$SiO_x$ structures, is applied in our case. It has been reported in the previous work that the narrower size distribution can be achieved by using layered structures compared to the unlayered one [11, 14]. The a-Si:H/a-Ge:H multilayers are fabricated by a computer-controlled PECVD system and its structure is investigated by x-ray diffraction measurements. The results show that the interface between a-Si:H and a-Ge:H is flat and the sublayer thickness can be well controlled.

The multilayer samples are subsequently oxidized by using similar conditions as for unlayered samples. Figure 5 is the Raman spectra for samples oxidized for different times at 800 °C. It is found that only Ge–Ge and Ge–Si vibration modes can be identified in Raman spectra. Also, the FWHM of the Ge–Ge peak is changed a little after 30 min oxidation, suggesting that the average size of Ge clusters is not increased with further oxidation. The average size is estimated to be about 6.5 nm for a layered sample after 70 min oxidation at 800 °C. Figure 6 is the room temperature PL spectrum measured at the same conditions as in figure 4 for a layered sample after oxidation at 800 °C for 70 min. The present PL peak is around 2.2 eV and the PL intensity is more stronger and the line width is quite narrow (FWHM is estimated to be about 0.3–0.4 eV) compared with the PL from unlayered samples, which maybe results from the narrower size distribution of nc-Ge.

It has been reported that Ge nanocrystals excited by an $Ar^+$ laser with a 488 nm line can emit the luminescence centred at 2.2–2.3 eV [10], and the radiative recombination of excitons confined in the Ge nanocrystals has been suggested as an origin of this visible light emission. In our case, the PL signals cannot be observed from the as-deposited samples, and after oxidation, the weak PL signals can be detected under $Ar^+$ laser irradiation, suggesting the visible light emission should be related to the formation of nc-Ge and the oxidation process. On the other hand, the PL intensity is gradually increased with increasing oxidation time both for unlayered and layered samples while the PL peak keeps the same independent of the starting materials and oxidation time. It is unlikely that the radiative recombination process is due to the recombination of excitons confined in nc-Ge. The possible mechanism of this orange–green emission can be attributed to the states existing in the nc-Ge/SiO interfaces or/and the $SiO_x$ matrix itself. In other words, the formation of nc-Ge makes the energy band of bulk Ge blue-shift to the visible light range; the photo-excited carriers in nc-Ge will be trapped by
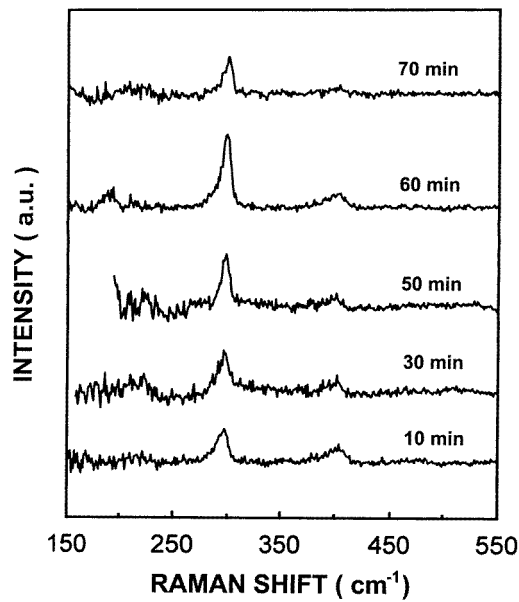
**Figure 5.** Raman spectra for a-Si:H/a-Ge:H multilayers oxidized at 800 °C for different wet oxidation time.
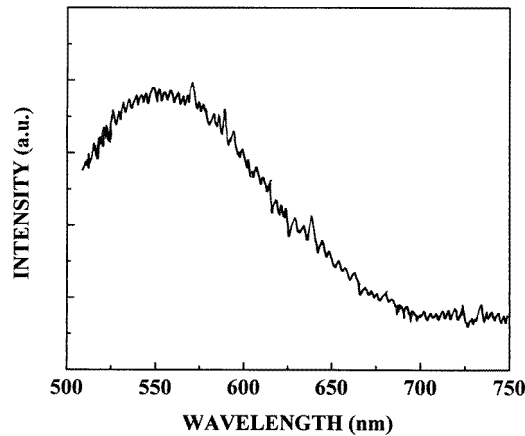


**Figure 6.** Room temperature photoluminescence spectrum for a-Si:H/a-Ge:H multilayers oxidized at 800 °C for 70 min.

defect states in the interfaces or/and in $SiO_x$ layers and emit the orange–green light through radiative recombination process. Thus, the PL peak is almost unchanged with different nc-Ge size and only the PL intensity is changed with different oxidation time.

## 4. Summary

In summary, nc-Ge embedded in $SiO_x$ matrix has been prepared by using starting materials of unlayered a-SiGe:H films and a-Si:H/a-Ge:H multilayers. The oxidation induces the precipitation of Ge clusters with nanometre size, and oxygen is bonded to Si to form an

$SiO_x$ matrix. Further oxidation will result in the oxidation of Ge clusters. Room temperature orange–green light emission could be observed and the PL peak is centred at 2.2 eV, which is independent of the oxidation time and starting materials. Compared to the unlayered samples, PL from layered samples has a narrower bandwidth and high signal-to-noise ratio. In contradiction to the simple quantum size effect model, recombination through the states in nc-Ge/$SiO_x$ interfaces and/or in the $SiO_x$ host matrix are suggested as the PL origin in our case.

## Acknowledgments

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