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Phonon Participation in the Light Emission Process of Porous GeSi Layer

SHI Hongtao, ZHENG Youdou, YUAN Renkuan
Department of Physics, Nanjing University, Nanjing 210008

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Relaxed $Ge_{0.5}Si_{0.5}/Si$ heterostructure was grown by the rapid radiant heating, very low pressure chemical vapor deposition (RRH-VLP/CVD). We report the anomalous temperature dependence of photoluminescence (PL) from porous GeSi layer at 77–300 K. The peak-emission energy of PL spectra from porous GeSi layer decreases with increasing temperature while its peak intensity rises, which is quite different from the temperature dependence of porous Si layer. Such dependencies are reversible and independent of temperature-change directions. No obvious 480 cm^{-1} peak was observed in Raman spectrum, indicating that no substantial amorphous phase contributes the intense light emission from the porous materials. We attribute such anomalous behavior of porous GeSi layer to phonon participation in the light-emission process of porous GeSi layer.

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As a consequence of indirect band gap semiconductor, monocrystalline Si emits very weak light with quite low quantum efficiency under normal circumstances. Recently, much attention has been paid to porous Si because it emits intense visible light at room temperature, which may revitalize the role of Si as an essential material for optoelectronics. However, the fragility of porous Si layer leads to the difficulty in obtaining direct and decisive TEM photographs to interpret such interesting and potentially important effects. Therefore several models have been proposed,[1–6] e.g. quantum-size-confinement effects, amorphous silicon layer contributions, large surface adsorption of contaminants, etc. But none of them is perfect and they still need further experimental demonstration.

Apart from the observation of light emission from porous silicon layer, photoluminescence of porous GeSi layer at T=12 K has also been reported by Gardelis *et al.*[7] recently, which lied in the higher energy side and was used as evidence for quantum confinement in photoluminescence (PL) of porous materials. Light emission was considered to be in agreement with the decay of excitons localized in structures of one or zero dimensions.

In this letter, we report for the first time the visible light emission and variable-temperature PL spectra at 77–300 K from porous GeSi/Si heterostructure fabricated by laterally anodization. Porous GeSi layer exhibits anomalous temperature dependence in comparison with that of porous Si layer. Raman spectrum at room temperature indicates that there is no substantial contributions of amorphous phase (a-Si) to the light emission. We attribute such anomalous temperature dependence of porous GeSi layer to phonon participation in the light-emission process of porous GeSi layer.

Relaxed $Ge_{0.5}Si_{0.5}$/Si heterostructure was grown by rapid radiant heating, very low pressure chemical vapor deposition (RRH/VLP-CVD), as described elsewhere.[8,9] The starting material used to grow relaxed GeSi/Si heterostructure was p-type (100) oriented single crystal Si, cleaned by RCA process. After the substrate was loaded into the chamber, Ar^+ sputtering was adopted to eliminate the oxide layer on its surface. The growth pressure and temperature were 1 mTorr and 600°C, respectively. Thickness of the epitaxial relaxed $Ge_{0.5}Si_{0.5}$ alloy layer was 240 nm, and it was not intentionally doped during growth.

Porous GeSi/Si heterostructure was fabricated by laterally anodization.[10] The electrolyte was 99.5 wt.% ethanol and 40 wt.% HF (1:1 by volume), a power supply being utilized as a constant current source. GeSi/Si heterostructure worked as anode and a Pt cathode. The anodizing current density and reaction time were 20 mA/cm^2 and 10 min, respectively. During the anodizing process, the sample surface was illuminated by a halogen lamp. The PL spectra were analyzed and recorded by a monochromator, a photomultiplier and a recorder. Excitation was by the 488 nm line of an unfocused Ar^+ laser with the incident power of 20 mW. Porous GeSi/Si heterostructure sample was mounted on the cold finger of a closed-cycle refrigerator with a temperature range of 77 to 300 K. The temperature shown in this letter is that of the specimen with laser working, and has an accuracy of 1 K, which may be slightly higher than the true temperature on the sample surface due to the laser-induced thermal heating and poor thermal conductivity of the porous material. The base pressure of the chamber was 1×10^{-5} Torr.

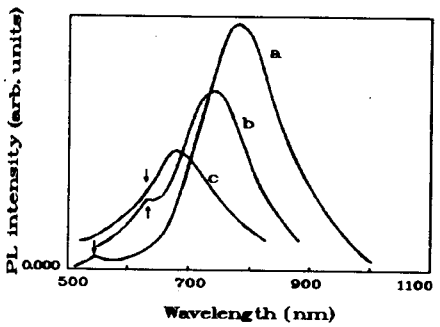

Fig. 1: Variable-temperature PL spectra from porous GeSi/Si heterostructure. a—81 K, b—198 K, c—300 K.

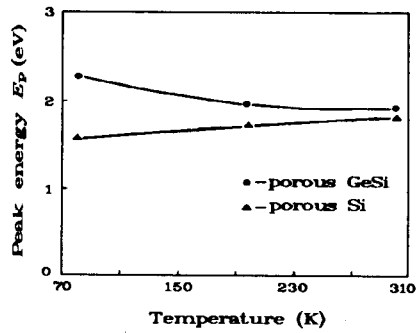

Fig. 2: Peak-emission energy of PL spectra of porous GeSi and Si layer as a function of sample temperature.

Figure 1 shows the PL spectra from porous GeSi/Si heterostructure sample under different temperatures covering a range of energies from near-IR to visible. Curve a is the PL spectrum at 81 K; curve b corresponds to that at 198 K and curve c at room temperature (300 K). It can be seen that except the ordinary red (or near IR) light emission peak from porous Si layer in the specimen, there exists another small peak at higher energy, which is in quite good agreement with Gardelis's experimental results[7] and is considered to be originating from the visible light emission of porous GeSi layer.

At room temperature, the small peak is not very clear because of the intense luminescent signal from porous Si layer. When the measurement temperature increases, the small peak moves to lower energy and its intensity rises. As shown in Figs. 2 and 3, porous GeSi layer has quite different temperature dependence from that of porous Si layer that when the temperature increases, the peak energy of PL spectrum from porous Si layer shifts upwards and the peak-emission intensity decreases, which was considered to be related to the enhancement of exciton recombination at low temperature. That is to say, with increasing temperature, the light-emission peaks of porous GeSi and Si layer shift to reverse directions, leading to the decrement of energy difference between the two peaks.

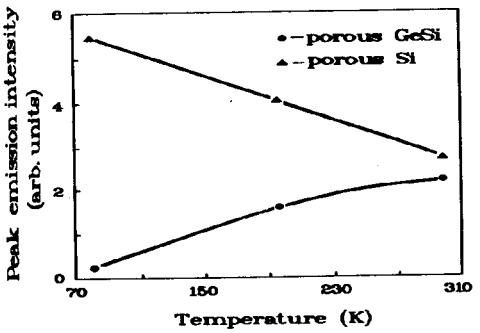

Fig. 3: Peak intensity of PL spectra of porous GeSi and Si layer as a function of sample temperature.

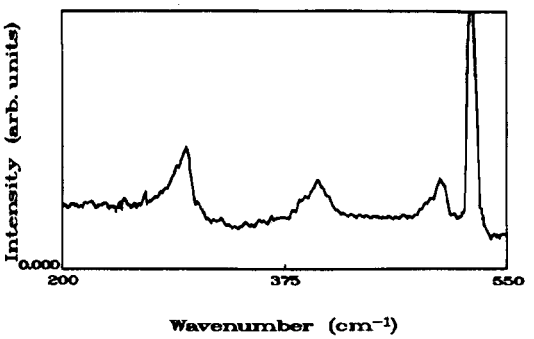

Fig. 4: Raman spectrum of the anodized porous GeSi/Si heterostructure sample at room temperature.

Figure 4 shows the Raman spectrum of the laterally anodized porous GeSi/Si heterostructure at room temperature. There was no additional peak at 480 cm^{-1} in Raman spectra related to amorphous phase (a-Si) which indicated that such light emission could not result directly from negligible amorphous phase contributions.

The variable temperature PL spectroscopy technique provides a valuable tool to study recombination of carriers, excitons, etc. Of course, it is helpful to clarify the origin of photoluminescence from porous Si and GeSi layer. If the light emission is related to quantum size confinement effects, porous Si and GeSi layer should have the same temperature dependencies since Si and Ge are semiconductors with similar properties except their different effective masses of carriers. The new anomalous temperature dependence of porous GeSi layer may be explained by phonon-assisted indirect transitions, which depends on the periodicity of the crystal lattice or microstructure. For porous GeSi layer, the average distance between pores or the pore density is responsible for such anomalous dependence. As the measurement temperature is lowered, the number of available phonons is decreased which reduces the light emission intensity from porous GeSi layer.

In summary, we reported for the first time the variable temperature photoluminescence of porous GeSi layer which showed different temperature dependence from that of porous Si layer in porous GeSi/Si heterostructure. No amorphous contribution to

the light emission was observed. Phonon participation was attributed to be responsible for such anomalous temperature dependence of porous GeSi layer, rather than quantum-size- confinement effects.

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