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Emission Evolution of α-Silicon Nitride Nanowires with Temperature

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The photoluminescence and temperature dependent emission spectra of silicon nitride nanowires were investigated by using femtosecond pulse laser. Three discrete sharp emission peaks were observed in photoluminescence, which were significantly different from that pumping by low excitation intensity laser. The temperature effects on emission peak energy were extracted using Gauss function, and should be attributed to volume-temperature effect and phonon effect.

Keywords: Silicon Nitride, Nanowires, Photoluminescence, Temperature.

1. INTRODUCTION

Silicon nitride is one of the most important materials in microelectronics and optoelectronics[1–4] due to its wide-band-gap semiconducting behavior with excellent thermo-mechanical properties and chemical inertness. However, numerous paramagnetic-resonance studies demonstrated that intrinsic defects (silicon dangling bonds, nitrogen dangling bonds and nitrogen lone pairs) abundantly existed in Silicon nitride.[5–10] The intrinsic defects in Silicon nitride primarily determine the electronics properties.[2,5,6] Meanwhile, such defects can serve as irradiative centers to provide intensive and broad band visible emissions,[11–14,24] whose spectra cover the whole visible light range, so it is a promising candidate for optoelectronic application such as irradiative elements in thin film light-emitting devices[3] or optical microcavity.[1,4] In some previous works, the researchers mainly focused their objectives on nonstiochiometric amorphous silicon nitride for optical properties studies, especially on photoluminescence.[3–4,11,12,14–16] Photoluminescence measurements on amorphous silicon nitride reported before are strongly dependent on fabrication conditions, stiochiometry and experimental setup. Researchers[12] have tried to correlate the luminescence and dangling bond paramagnetic signal to show that the defects were corresponding to the irradiative process although it is very difficult to identify undoubtedly the nature of emission. however, luminescence measurement technology still can be considered as a powerful tool of insight into the nature of electronic state process in various types of silicon nitride.[13,17]

In recent years, one-dimensional nano-structure crystalline silicon nitride such as nanobelts and nanowires developed quickly.[17–21] Optical spectral analysis technologies have been applied on silicon nitride nanobelts[17,26–28] to recognize the electronic state corresponding to the intrinsic defects in Si_3N_4 nanocrystal.[26] Emission from nanocrystal was supposed to be relative to the silicon and nitrogen dangling bonds in Si_3N_4. The dangling bonds have three charged states: positive charge, negative charge and neutral center, which are metastable. Especially, the nitrogen dangling bonds (N center) depend on the temperature and annealing for existence.[9,10,25] So it can be predicted that the dangling bonds related photoluminescence is highly dependent on extrinsic condition such as temperature.

In this work, we present the photoluminescence and its temperature dependence on silicon nitride nanowires. In attempt to set an insight of the defects corresponded, we try to study the relationship of photoluminescence and temperature.

2. EXPERIMENTAL DETAILS

Crystalline Silicon Nitride nanowires (Si_3N_4 NWs) were synthesized by catalyst-assisted pyrolysis from a polysilazane polymeric precursor. The synthesis technique process of silicon nitride nanowires followed our previous

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work[21] but with slightly higher growth temperature. The Si_3N_4 NWs were treated at 600 °C for half an hour in air then cooled to RT. The Si_3N_4 NWs were characterized by using scanning electron microscope (SEM) and X-ray diffraction (XRD).

Photoluminescence of α-Si_3N_4 nanowires was recorded by spectra-pro 2300i equipped with liquid nitrogen cooled CCD. Si_3N_4 nanowires were dispersed on copper-holder wafer and mounted in cryostat, in which temperature can be adjusted in a range of 5 K to room temperature (RT). Excitation sources were a frequency-doubled 1 kHz Ti: sapphire regenerative amplified laser, which can output 120 fs pulse with energy of 200 μJ at 395 nm.

3. RESULT AND ANALYSIS

The morphology of Si_3N_4 NWs was observed under SEM. Figure 1 exhibits a representative SEM image of Si_3N_4 nanowires, which have a cylindrical shape with more than 1 μm long and 100–200 nm wide. The nanowires revealed fairly uniform in diameter along the wire axle. The XRD pattern of Si_3N_4 NWs (Fig. 2) suggested a pure α-Si_3N_4 phase.

Intensive luminescence of silicon nitride nanowires can be observed at room temperature under the excitation of frequency doubled Ti: sapphire laser. As shown in Figure 3, the emission spectrum was consisting of three sharp emission peaks which were located at 673 nm (1.84 eV), 596 nm (2.08 eV) and 419 nm (2.96 eV). The line width of emission peaks were less than 9 nm. Previous studies have reported that the typical photoluminescence of α-Si_3N_4 nanocrystal with the excitation of CW laser or Xe-lamp revealed a broad emission band ranging from 400 to 800 nm centered at ~600 nm[17, 21, 26, 28] or ranging between 360–480 nm centered at 406 nm.[27] Cathodoluminescence (CL) spectra of Si_3N_4 nanowires has also been reported,[30] and consist of three broad bands centered at 305 nm, 540 nm and 735 nm, respectively. The photoluminescence obtained in our experimental setup revealed

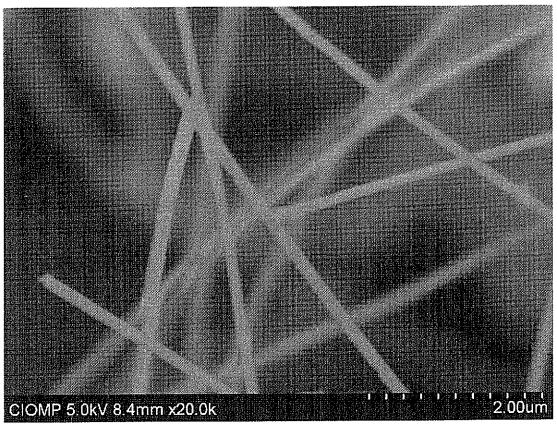

Fig. 1. SEM image of Silicon nitride nanowires.

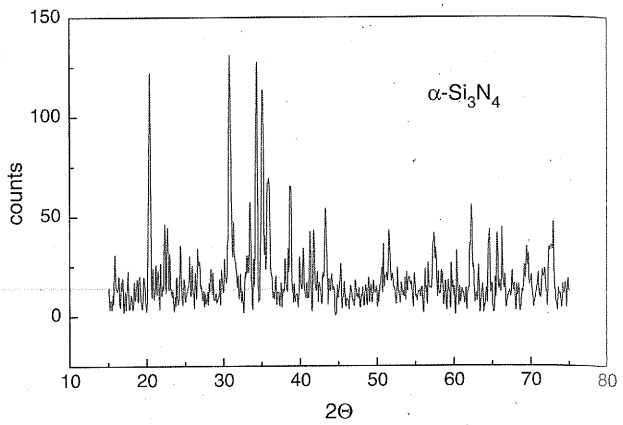

Fig. 2. XRD pattern of α-Silicon nitride nanowires.

three sharp emission peaks, which had a far difference from spectral feature of α-Si_3N_4 nanocrystal reported previously. This is due to the high intense excitation condition with peak power of nearly 2 GW. The emission spectral narrowing should be resulted from the amplified spontaneous emission (ASE) induced by ultrashort pulse high intensity pump. ASE were observed in many kinds of semiconductor nanocrystal such as (Cd, Zn)Se nanoparticles at excitation energy density exceeding a threshold that induced average electron–hole pairs more than 1 in each quantum dot.[29] The ASE in semiconductor nanocrystal was involved in biexciton or multiexciton process.

Previous studies reported that the broad emission from α-Si_3N_4 nanocrystals was divided into three discrete broad emission bands centered at about 1.83 eV, 2.36 eV and 3.01 eV respectively,[26] by using Gauss line-shape peak function simulating. In general, the origin of the emission was ascribed to the transition among silicon nitride defects. A number of electron-paramagentic-resonance studies on amorphous silicon nitride, α-Si_3N_4 and α-SiNx thin film have demonstrated that Si dangling bonds $N_3 \equiv Si^*$ (named as K center) and Nitrogen dangling bonds $Si_2 = N^*$[6–9]

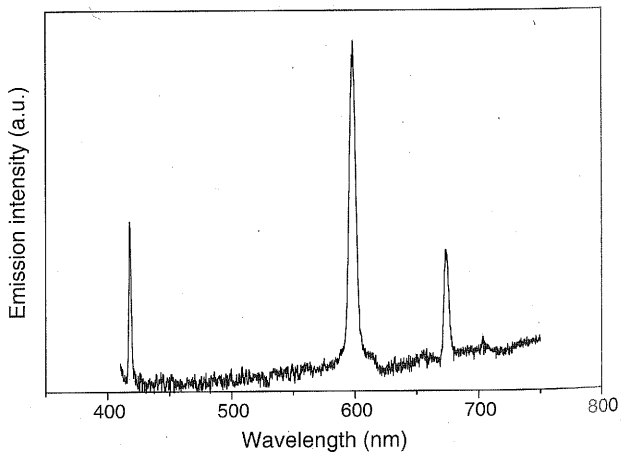

Fig. 3. Emission spectra of Silicon nitride nanowires excited by Ti: sapphire 120 fs pulse laser of 395 nm at room temperature.

(named as N center) in silicon nitirde. K^0 center and N_2^0 center have opportunity to capture electrons or holes to form charge centers. The electron paramagnetic studies of dangling bonds demonstrated that more charged centers are more stable in comparison with neutral one in amorphous stoichiometric silicon nitride.[5] These states of centers was associated with the irradiative transition.[26] The emission peaks in Figure 3 should be accordance with the transition energy occurring among the defect states. To character the emission, the peak central energy and linewidth of photoluminescence spectra were extracted utilizing Gauss line-shape peak function. The three emission peaks were centered at 1.84 eV, 2.08 eV and 2.96 eV, with linewidth of 9 meV, 17 meV and 24 meV respectively.

To gain an insight into the characteristic of the irradiative center, the temperature dependent photoluminescence of α-Si_3N_4 NWs was carried out under a equivalent excitation power. Figure 4 showed the emission spectra of α-Si_3N_4 NWs at different temperatures ranging from 5 K to 300 K. The discrete emission peaks above revealed a slight shift in peak energy and a line-broadening with temperature increasing in a experimental temperature range. The intensity of their emissions had a strong temperature dependence, and diminished with temperature increase from 100 K to RT. However, the intensity was affected by complex factors, so we did not study it in this work.

The emission spectra were characterized by the peak central energy and linewidth by fitting the multiple-peaks photoluminescence using Gauss type distribution function.

Peak emission energies of Si_3N_4 NWs of the peaks at about 673 nm and 596 nm were plotted as a function of temperature in Figure 5. Emission central energy for low energy emissions reveals a monotonically blue shift with temperature changes in the entire experiment if the experimental error and mathematical error are considered. The

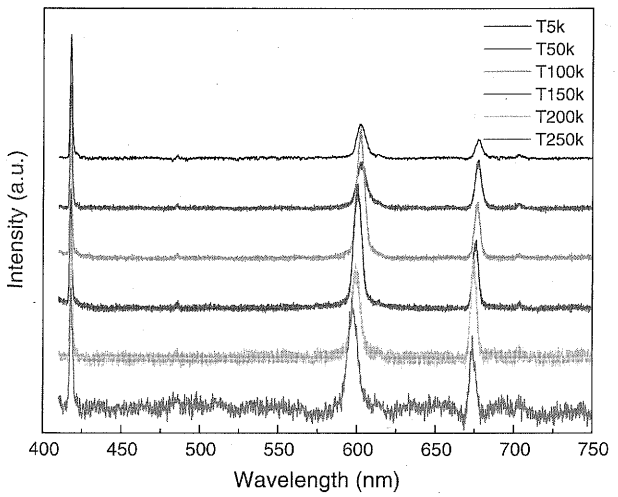

Fig. 4. Photoluminescence of Silicon nitride nanowires excited by 120 fs pulse laser under various temperatures ranging from 5 K to 300 K.

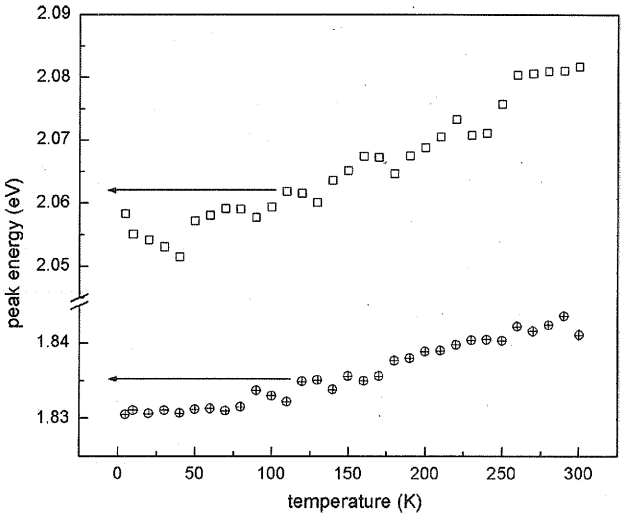

Fig. 5. Peak energy of emission peaks corresponding to 673 nm (1.84 eV), and 596 nm (2.08 eV) were plotted as a function of temperature.

other one at high energy side takes a completely different change with temperature. It keeps a certain value at low temperature, and then a slightly reducing of emission energy occurs from 100 k. The temperature dependent coefficient α can be expressed by the following equation

$$\alpha = \frac{\partial E_i}{\partial T}$$

Here E_i is emission central energy, T is experimental temperature. α is 0.06 meV/K for emission at about 1.84 eV, and 0.12 meV/K for 2.08 eV. However, the temperature dependent emission peak at 2.96 eV has a different behavior. The peak at 2.96 eV shift slightly and negatively in comparison with the others, as observed in Figure 4. Thus, the energy levels of defect states should have a different temperature dependence coefficient due to volume–temperature effect and phonon effect.

The phonon effect also influences the emission linewidth broadening with temperature. The linewidth broadening in general is consisted of inhomogeneous and homogenous term.[31] The inhomogeneous broadening is due to the fluctuations of circumstance such as size or composition, which is independent on temperature. The homogeneous term is mainly caused by the exciton/electron and phonon interaction, which increases monotonically with temperature. The behavior of temperature dependence of peak linewidth at 2.08 eV and 2.96 eV is a typical inhomogeneous broadening by electron-phonon interaction. But the emission at 1.8 eV is almost independent on temperature. The difference of temperature dependent line-broadening of three emission peaks imply that electron-phonon interaction is constrained in defect center corresponding emission peak at 1.8 eV.

4. CONCLUSION

Amplified spontaneous emission occurred in α-Si_3N_4 nanowires under excitation of 120 fs pulse laser at energy of 200 μJ. Three discrete sharp peaks were observed in photoluminescence of α-Si_3N_4 nanowires. The emission peak energy and linewidth developed with temperature and the temperature effect was due to the co-affecting of volume–temperature and phonon effect.

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