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Structural evolution of SiN_x films deposited by ECR and its light emission

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Abstract

Structural and optical properties of a-SiN_x films deposited by electron cyclotron resonance chemical vapor deposition (ECRCVD) have been investigated. The Fourier transform infrared (FTIR) spectroscopy shows the structural evolution of the SiN_x films, which are defined as Si-rich SiN_x and N-rich SiN_x films, also confirmed by Raman spectroscopy. The origin of the light emission for SiN_x films may be attributed to two mechanisms, i.e., quantum confinement effect (QCE) and transition of defect energy levels. The correlation between light emission and structures of SiN_x films is discussed.

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Keywords: ECRCVD; SiN_x; FTIR; Light emission

1. Introduction

Light emission from Si-based materials is an important research area for potential optoelectronic applications compatible with current VLSI silicon technology. Ever since the report of luminescence by Canham et al. [1], nanocrystal Si (nc-Si) has been the subject of intensive research. In particular, silicon-rich silicon oxide, which consists of nc-Si embedded in a host matrix, has attracted much attention due to its ability to produce a robust, well-passivated nc-Si film. However, post-annealing at temperatures over 1100 °C is required for the formation and crystallization of silicon nanoparticles in SiO_x to get a high-efficiency photoluminescence (PL) [2]. Recent researches [3,4] have showed that it is difficult to obtain visible luminescence from Si-rich SiO_x even with a sufficiently strong quantum confinement effect (QCE) in the nm-sized nc-Si. On the other hand, some experiments [5,6] with nitride surface passivation for nc-Si in SiN_x have been carried out, and have shown that the light emission peaks are similar to those of SiO_x, centering in the near-infrared region.

However, recent researches show that high-efficiency PL may arise from amorphous well-passivated silicon nanoparticles in an SiN_x matrix. Park et al. [7,8] have observed a strong tunable luminescence by controlling the size of amorphous silicon quantum dot embedded in the SiN_x matrix deposited by plasma-enhanced CVD (PECVD). Wang et al. [9] have prepared the same alloys by PECVD from SiH_4 and N_2 to get a PL center energy tunable from 2.0 to 2.9 eV, depending on the silicon nanoparticle size. But the origin of PL from a-SiN_x is still a matter of debate. For example, Gritsenko et al. [10] explained the visible PL near the UV region in a-SiN_x thin films by the spatial variation of chemical composition in SiN_x. Zhang et al. [11] have reported that light emission in single-crystalline a-Si_3N_4 nanobelts is due to the intrinsic and defect energy levels. Despite the controversy, the above-mentioned investigations may indicate that amorphous nanoclusters are not necessarily bad light emitters. More recently, Cho et al. [12] have fabricated light-emitting diodes using n-type SiC/SiN_x/p-type Si heterojunction and high-efficiency visible electroluminescence at 2.4 eV has been observed.

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Electron cyclotron resonance PECVD has already been shown to be a very versatile deposition technique with potential application to a-SiN_x [13]. Compared with conventional RF-PECVD, it has some advantages in depositing a-SiN_x films, such as higher gas ionization, higher plasma density, lower pressure, lower-temperature operation, etc. Additionally, it can provide the growing a-SiN_x film with low-energy ions for hydrogen removal. In this present work, we will show the correlation between light emission and structural evolution of SiN_x films grown by ECRCVD method. The ratio of Si and N in the films was controlled by introducing flow rate ratios of NH_3 and SiH_4 diluted with Ar. Structural evolution and optical absorption were characterized by FTIR, Raman and UV–VIS spectroscopy, respectively. PL spectra were measured using the 325 nm line of a He–Cd laser.

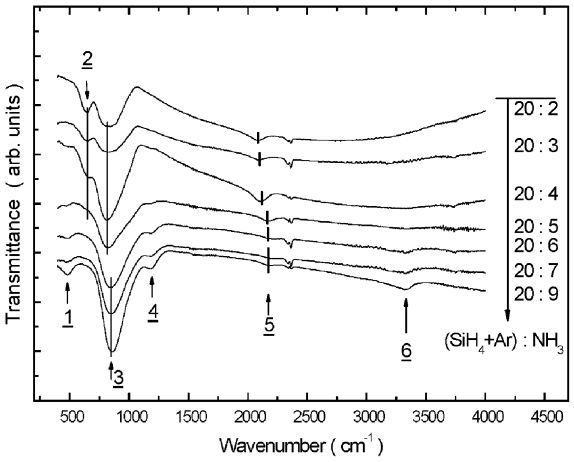

Fig. 1. FTIR spectra of SiN_x films on KBr with variable NH_3 flow rate.

2. Experimental

a-SiN_x thin films used in this work were prepared on Si(1 0 0) wafers, Ge(1 0 0) wafers, KBr wafers and quartz, respectively, by an ECRCVD system using the gas mixture of NH_3 and SiH_4 (80% Ar-diluted). The detailed experimental setup can be seen elsewhere [14]. The flow rate of SiH_4 was fixed at 20 sccm, while NH_3 flow rate was varied between 2 and 9 sccm. NH_3 gas was injected upstream to the ECR region while the SiH_4 was introduced downstream through a gas dispersal ring. For all the processes of film deposition, the microwave input power and the total pressure were kept at 600 W and 0.5 Pa, respectively. The infrared absorption spectra were measured with a Nicolet-550 spectrometer. The PL measurement at room temperature was excited with 325 nm from a He–Cd laser. Optical band gap was deduced from the measurement of transmittance and reflectance for SiN_x films.

3. Results and discussion

Structural investigation for the as-deposited SiN_x films on KBr wafers was carried out by means of FTIR technique, as shown in Fig. 1, with an increase of NH_3 flow rate R from 2 to 9 sccm and a fixed SiH_4 flow rate of 20 sccm. In the spectra, a main peak labeled as 3, centering at about 850 cm^{-1}, corresponds to Si–N stretching vibration mode. The absorption intensity of this feature enhances and the peak has a tendency to shift toward a higher wave number (blue shift) with the increase of R. Another peak (labeled as 5), which corresponds to Si–H stretching vibration mode around 2190 cm^{-1} also shows a clear blue shift. The reason for blue shift of Si–N and Si–H mode with the increase of R is that the Si atoms are bonded to more N atoms, which have electronegativity larger than H. At a low value of R, no feature at around 3350 cm^{-1}, characteristic of the N–H bond, is observed. This is because of the exothermic chemical reaction Si–Si + N–H → Si–H + Si–N, namely, the formation of Si–H and Si–N bonds is favored at the expense of Si–Si and N–H bonds [15]. As NH_3 flow rate is more than 6 sccm, N–H stretching mode appears at 3350 cm^{-1}, accompanying with N–H wagging mode (labeled as 1) and N–H bending mode (labeled as 4). This is due to the excess N–H bonds reacting with Si–Si bonds at the film surface. From the above-mentioned simple film growth kinetic model, two kinds of as-deposited SiN_x films may be classified: one is Si-rich SiN_x films with R less than 6 sccm, and the other is N-rich SiN_x films with R larger than 6 sccm. This classification can be confirmed by a peak, labeled as 2, centered at 648 cm^{-1} in the infrared spectra. This feature can be assigned to the wagging mode of the $HSi–Si_3$ [16], where a blue shift of 17 cm^{-1} occurs compared to the same mode of bulk Si crystal at 631 cm^{-1}, due to the H passivation and structural disorder of Si clusters in SiN_x film. At a low flow rate of NH_3, Si–Si shoulder peak near the Si–N mode appears clearly, while with the increase of R, the intensity of Si–Si mode decreases gradually, indicating a transition from Si-rich region to N-rich region.

The structural evolution of SiN_x films at a low R is indicative of an enhanced phase separation of Si and silicon nitride in the deposits. The presence of Si cluster can be confirmed by Raman scattering spectroscopy. In order to avoid Raman disturbance from Si substrate, Ge(1 0 0) wafers are used for deposition of SiN_x films, Raman spectra are shown in Fig. 2. It can be found that there exist four Raman peaks from a-Si, TO mode located at 480, TA mode at 180, TO + TA mode at 620 and 2TO mode at 920 cm^{-1}. These peaks indicate that Si clusters in SiN_x are typically amorphous. Disappearance of these acoustic peaks with R more than 6 sccm also shows the transition of SiN_x films from Si-rich region to N-rich one.

Since the luminescence efficiency in well-prepared bulk amorphous silicon is higher than that of bulk crystalline silicon due to its structural disorder, a-Si is believed to be a good candidate for short-wavelength light emitters [17,18]. Fig. 3 shows PL behaviors of SiN_x films with different NH_3 flow rates. No clear PL peaks can be seen for the Si-rich SiN_x films with R less than 3 sccm. This may be due to a