

Optical and morphological properties of SiN_x/Si amorphous multilayer structures grown by Plasma Enhanced Chemical Vapor Deposition

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Very thin layers of Si were grown in between silicon nitride layers using Plasma Enhanced Chemical Vapor Deposition (PECVD) technique and SiH₂Cl₂/H₂/NH₃ mixtures. Deposition conditions were selected to favor Si cluster formation. Room Temperature Photoluminescence (RT-PL) and optical transmission in different ranges were used to evaluate the optical and structural properties of the films. Scanning Electron Microscopy (SEM) of the cross section of cleaved samples allowed to observe a clear pattern of Si clusters embedded in the SiN matrix. The UV-VIS absorption spectra present two band edges. We assume that the higher band gap is due to the amorphous Si clusters. RT-PL spectra are characterized by two broad bands: one centered at 1.5 eV and the other at 2.1 eV. The broad luminescence centered at 2.1 eV could be associated with the higher band gap observed in absorption spectrum. After vacuum annealing of the samples at 400 °C, the band at 2.1 eV disappears.

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1 Introduction

Luminescence from silicon-based materials prepared using different techniques has been extensively studied recently due to its potential application in both nanoelectronic and photoelectronic devices [1–3]. Notably, superlattices composed of alternating nc-Si and SiO₂ or SiN_x layers have been given much attention due to a large volume fraction of nc-Si and the controllability of the size and density of nc-Si clusters. In PECVD techniques, the properties of the films are much influenced by hydrogen atoms; hydrogen and hydrogen-related bonds are critically associated with the surface passivation, the etching reaction, and the modification of Si–Si networks [4]. The luminescent emission from crystalline and amorphous Si nanoclusters embedded inside or between layers of larger gap materials, such as silicon oxide or silicon nitride, covers a wide wavelength range from the infrared (IR) to the ultraviolet-visible (UV-VIS) region. In general, the origin of such luminescence is thought to be due to Si quantum confinement. However, many features of the optical emission and properties of these materials, as well as the role of surface and/or interfaces between nanoclusters and matrix are still controversial and need to be clarified. Among the different mechanisms proposed for the radiative recombination processes the most likely ones are related to the direct band-to-band recombination (usually named “quantum confinement

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models''-QCM, because the emission features strongly depend on the size of the nanostructures [5, 6]) and the exciton recombination via interface luminescent levels (usually called ''surface recombination models''-SRM [7, 8]). In the present work, layers (or fractional layers) of Si were grown in between silicon nitride layers by using Plasma Enhanced Chemical Vapor Deposition (PECVD) technique and $\text{SiH}_2\text{Cl}_2/\text{H}_2/\text{NH}_3$ mixtures. The origin of the luminescence is studied by using FTIR absorbance spectra in the as-grown and annealed samples. The identification of hydrogen related bond types present on the nanoclusters surface as well as the understanding of the fundamental kinetics of the surface passivation are essential in the understand of the photoluminescence origin.

2 Experimental details

The silicon nitrides and silicon nanocluster SiN/Si multilayers were prepared using a conventional PECVD system, with parallel-plates 150 cm^2 in area, 1.5 cm apart, and activated by a 13.56 MHz RF signal. The films were deposited on high resistivity silicon, fused silica and corning glass, for their structural and optical characterization, respectively. The substrates were subjected to a standard cleaning procedure and in the silicon case, were also etched in diluted hydrofluoric acid (5% HF) immediately before loading them into the deposition chamber. Dichlorosilane and ammonia were used as precursor gases, with argon and hydrogen as the diluent gases. In all cases the deposition pressure and substrate temperature were kept constant at 500 mTorr, 200 °C respectively. The multilayer structure consists of 12 cycles of silicon nitride thin films with silicon layers in between. The silicon nitride thin layers were grown with a $[\text{NH}_3]/[\text{SiH}_2\text{Cl}_2]$ flow ratio of 2.5 and a growth time of 1 min. The silicon layers were grown with SiH_2Cl_2 and H_2 flows rates of 2 sccm and 20 sccm, respectively. The growth time was 30 seconds in all cycles. A Gaertner L117 Ellipsometer equipped with a He-Ne laser ($\lambda = 632.8\text{ nm}$) was used to measure the refractive index and thickness of the films. The bonding structure of the films was analyzed by means of a Fourier Transform Infra-Red (FTIR) spectrometer (Nicolet-210). The XPS analysis of the structure profile was made by means of a VG Microtech Multilab ESCA 2000 system, equipped with a hemispherical-multichannel detector CLAM4-MDC. The spectra were obtained using the $\text{MgK}\alpha$ ($h\nu=1253.6\text{ eV}$) X-ray source, operated at 15 kV and 20 mA. Erosion of the surface was performed using Ar ions. Photoluminescence studies were carried out at room temperature in a conventional PL-system described deeply elsewhere [9]. An Argon⁺ laser tuned at 4880 \AA was employed as the excitation source, with a mean power density of 120 W/cm^2 . The outgoing radiation from the sample was focused on the entrance slit of a 1403-SPEX double monochromator. The detection was carried out using a RCA-C31034 photomultiplier (PM) thermoelectrically cooled coupled to a photon counter. All the spectra were corrected for the spectral response of the system.

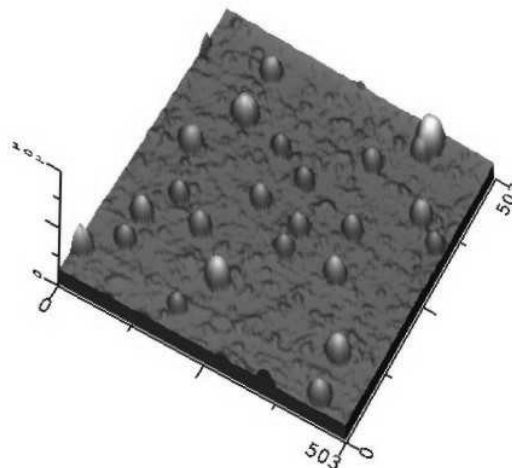


Fig. 1 The AFM image shows the surface morphology of SiN exposed to Si for 30 s. (The units are nm in the axis parallel to the surface and nm in the axis normal to the surface.)

3 Results and discussion

The AFM image in the Fig. 1 shows the formation of Si clusters for a sample in which SiN surface was exposed to Si for 30 s. As can be observed, the distributions of clusters are homogeneous and are nano-size. Figures 2 and 3 show a Scanning Electron Micrograph of the cleaved surface of the multilayer

structure and a XPS profile, respectively. Both figures show the evidence of the multilayer structure the type SiN_x:H/a-Si/SiN_x:H. Taking into account the morphology of the single not covered Si layers, we expect the Si regions in the multilayer are not completed layers, but formed by Si clusters. A room temperature (RT) PL spectrum of the as-grown sample is shown in Fig. 4. It shows two bands: one weaker centered at around 1.5 eV and another stronger at 2.13 eV. Quantum confinement effect enlarges the band-gap of nanoclusters, increasing the oscillator strength and giving rise to efficient and visible luminescence. There have been suggestions that a distribution of the nanoclusters size may be responsible for the broad PL spectra of the nc-Si:H thin films, which typically exhibits a FWHM of 300–400 meV, and some attempts have been made to explain the effect of the size distribution on the PL spectrum [10]. Tauc plots of absorbance spectra for samples grown onto glass substrates are displayed in Fig. 5. Two distinct absorption edges can be observed corresponding roughly to the two emission bands in the luminescence spectrum. To investigate the origin of these bands, the sample was annealed in vacuum at 400 °C for 1 hour.

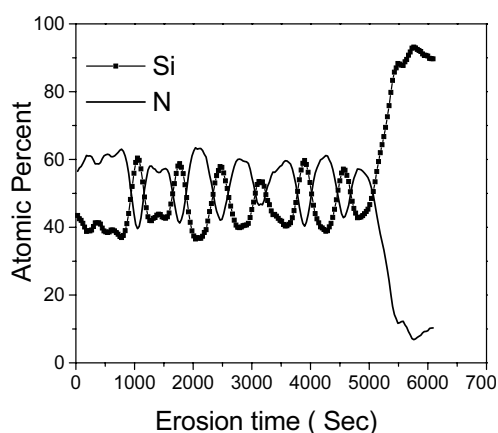


Fig. 3 XPS compositional profile of the SiN/Si multilayer.

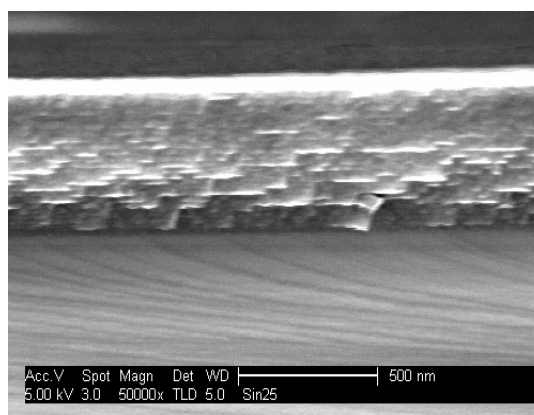


Fig. 2 Scanning Electron Micrograph of a cleaved surface of the SiN/Si multilayer.

The RT PL spectra for the annealed samples are also shown in Fig. 4. As can be seen, the stronger band at 2.13 eV disappeared after annealing. FTIR absorbance spectrum of both as-grown and annealed SiN/Si multilayers is shown in Fig. 6. A decrease (up to below the detection limit) in the peak related to the Si-H stretching mode ($2160\text{--}2220\text{ cm}^{-1}$) is observed in the annealed sample. The NH bonds concentration also decreases. This result is clarified in the insert of Fig. 6.

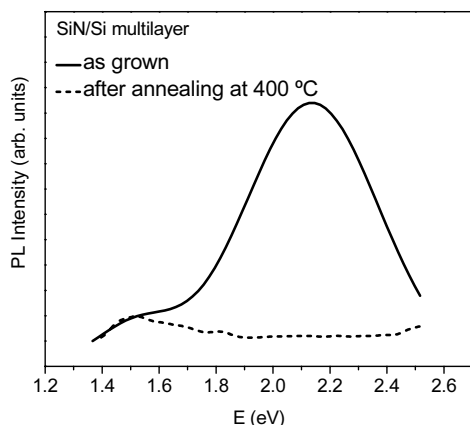


Fig. 4 RT-PL spectra for both as-grown and annealed SiN/Si multilayers.

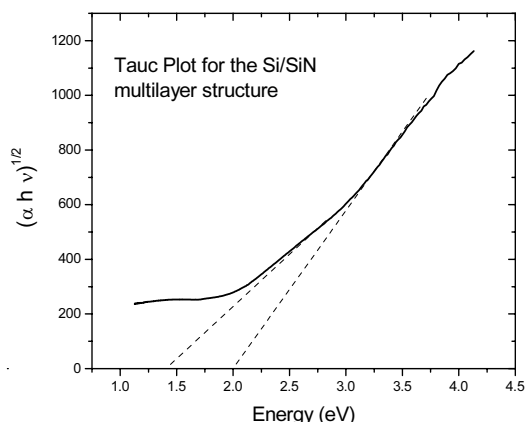


Fig. 5 Tauc plot of the absorbance spectrum of the multilayer structure.

The spectra shows that the peak assigned to the stretching vibration of Si–H bonds, i.e. a clustered monohydride made on the surface of the Si nanoclusters disappears. This indicates that Hydrogen effuses from the sample during vacuum annealing at 400 °C. Most of the hydrogen present in the as-grown multilayer structure is passivating the Si nanocluster surface [11]. After the annealing, large quantities of dangling bonds in the silicon nanocluster surface is created by hydrogen effusion and non-radiative recombination prevails. This explains the results of PL spectrum of these samples and demonstrates that the origin of the photoluminescence in these systems is due to the nanocluster confinement and not to superficial states [5, 7].

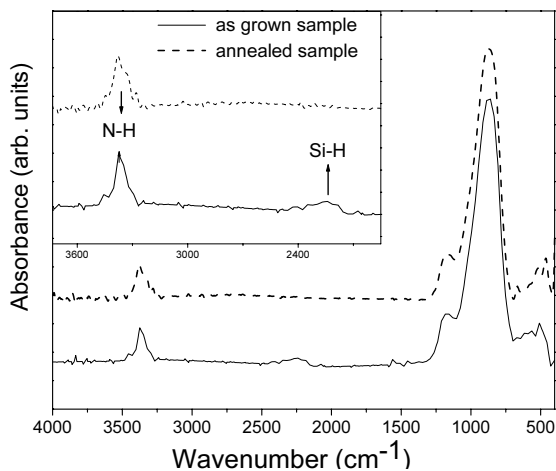


Fig. 6 FTIR absorbance spectra for both as-grown and annealed SiN/Si multilayers.

energy band is not clear but is presumably due to interface states or to Si-rich SiN_x in the neighborhood of the Si clusters.

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4 Conclusions

Multilayer structures of SiN_x/nc-Si:H/SiN_x were obtained by Plasma Enhanced Chemical Vapor Deposition. Room temperature luminescence shows two bands in the VIS-UV region. Two different gaps are also observed in the transmittance spectrum. The origin of the high energy band is considered to be due to quantum confined nc-Si. This peak disappears after vacuum annealing at 400 °C. Also, after annealing, the Si-H stretching mode (2160–2220 cm⁻¹) (as observed in FTIR spectroscopy) decreases. This can be explained by considering that Hydrogen atoms are passivating the dangling bonds of the Si cluster in as-deposited samples. After annealing, H effuses from the sample and non-radiative centers are responsible for the suppression of the luminescence. The origin of the low energy