PHOTOLUMINESCENCE AND OPTICAL FEATURES OF HYDROGENTED SILICON NITRITE THIN FILMS

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Abstract: In this work we report room-temperature photoluminescence from as-deposited hydrogenated silicon nitride films due to silicon nanocrystals/structural disorder. A systematic study of fabrication parameters and post-heat treatment on the optical features has been done. Enhancement in optical constant on annealing is attributed to phase separation into c-Si and other phases.

1. INTRODUCTION

The fabrication of active and passive optical devices for the optical communications requires selection of appropriate material. In this context, the light emission i.e photoluminescence from Si nanostructures [1] in dielectric such as SiO₂ (or Si₃N₄) as well as variations in optical constants [2] are of great interest. In this regard intense light emission silicon nanocrystals (Si-n) in SiO₂ systems have been extensively studied [3]. However, the extremely high potential barrier (~8.5 eV) of silicon dioxide (SiO₂) imposes the limitation on the injection of charge carriers and hence, efficient usage of such a composite is difficult for applications such as electrophotonic devices [4]. In such cases, hydrogenated amorphous silicon nitride (a-Si₃N₄:H) because of its low potential barrier (~2.0 eV) for carriers, can alleviate the carrier injection problem and hence is considered as a potential candidate for the development of silicon-based photonic devices [5]. However, key issues such as origin of light emission and dramatic changes in optical and structural features after thermal treatment were not yet clear. In this work, we have extensively studied, by varying the stoichiometry, post-heat treatment RTA (rapid thermal annealing) of hydrogenated amorphous silicon nitride (a-Si₃N₄:H) films on optical and structural features such as refractive index, photoluminescence, surface composition etc.

2. EXPERIMENTAL DETAILS

Hydrogenated amorphous silicon nitride (a-Si₃N₄:H) thin films with different stoichiometries were deposited on films on the n-type Si (100) substrate at 200 °C using Hg-sensitized Photo-CVD (chemical vapour deposition) with a 253.7 nm low pressure lamp. Silane (4% in argon) and ammonia were used as the precursor gases. To evaluate optical constants, namely the refractive index and extinction coefficient, spectroscopic ellipsometry was employed using a Sopra S-5 system to measure over the wavelengths from 250 to 900 nm with a glancing angle of 70°. Glancing angle x-ray diffraction (GAXRD) measurements were carried out using a Philips Expert Pro-PW model 3040 with Cu Kα (λ=1.5418 Å) radiation. Areal concentration of hydrogen (N_H in atoms cm⁻²) of both ASD and RTA treated films was measured by the elastic recoil detection analysis (ERDA) method using Ag⁺⁺ (100 MeV) ions. The x-ray photoelectron spectroscopy (XPS) was performed to analyze surface phase compositions in different stoichiometric films. The binding energy values are calibrated by using the value of contaminant carbon (C 1s=284.6 eV) as a reference. Raman scattering spectra were performed on Micro-Raman T64000 Jobin Yvon triple monochromator spectrometer using 514.5 nm line of argon laser. For Photoluminescence (PL) measurements samples were excited with a 405 nm semiconductor diode 30 mW and a power density 1 W/cm². The microstructure of the samples was analyzed by high resolution TEM (HRTEM: Technai G2) operated at 200 kV.

3. RESULTS AND DISCUSSION

Ellipsometry angles (Ψ, Δ) were recorded in the range of 300 to 850 nm [shown for sample 3, Fig. 1(a)]. Marquardt-Levenberg minimization technique was used to fit these angles to derive optical constant, refractive index (n), extinction coefficient (k) [shown for sample 3, Fig. 1(b)]. Three layer model was taken in order to get better agreement between the experimental and simulated data point. The top and bottom layer was taken as SiO₂ having thickness typically between in 12.6 and 23.2 nm and more or less constant (nearly 8.3 nm) after thermal treatment. The middle layer was taken as mixture of silicon nitride and amorphous/crystalline silicon [2]. Table 1 shows the values of refractive index and thickness obtained from the fitting experimental data. As expected increase in the silane flow rate results in increase refractive index, however a drastic change in the refractive index and thickness can be noticed on annealing (see table 1). The increase in refractive index is probably due to phase separation as a result of out-diffusion of hydrogen.
Table 1. Relevant parameters, refractive index \(n\), extinction coefficient \(k=0\) (at \(\lambda = 632.8\) nm) and thickness \(t\) obtained from ellipsometric analysis as a function of silane flow rate (all other deposition parameters are constant) for as-deposited and thermal annealed films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flow rate of silane (sccm)</th>
<th>As-deposited (n : t) (nm)</th>
<th>Thermal annealed (n : t) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>2.07 : 83.8</td>
<td>2.28 : 67.4</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>2.05 : 81.5</td>
<td>2.25 : 66.0</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>2.19 : 59.2</td>
<td>2.42 : 40.2</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>2.19 : 47.2</td>
<td>2.36 : 38.9</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>2.32 : 54.9</td>
<td>2.11 : 50.6</td>
</tr>
</tbody>
</table>

Substantial increase in the contribution of excess Si was found (from 10.5% to 21.7% for sample 3) in thermal annealed film as compared to the as-deposited film. Our optical study suggests the presence of excess silicon after annealing, which was also noticed in the GAXRD (not shown here). In addition to this to investigate the role of hydrogen content in phase separation, ERDA measurements were performed. The concentration of hydrogen (atoms/cm\(^3\)) as determined by ERDA in thermal annealed samples was found to be decrease in the range 0.42 to 0.65 \(\times 10^{22}\) atoms/cm\(^3\) as compared to the as-deposited samples (5.83 to 8.06 \(\times 10^{22}\) atoms/cm\(^3\)) [6]. The decrease in hydrogen concentration is clearly indicative of out-diffusion of hydrogen. Which further implies that on annealing the changes in optical constant occur due to bonding rearrangements predominantly between the Si-H (for silicon rich) and N-H (for nitrogen rich) bonds.

In order to confirm the phase separated individual silicon entities and to get further insight of surface composition x-ray photoelectron spectroscopy (XPS) was carried out. Figure 2 shows the Si 2p x-ray photoelectron spectrum of the as-deposited sample 3. According to procedure adopted by Kärcher et al [7] the Si 2p has been deconvoluted into five different peaks corresponding to different phases.

![Ellipsometry analysis](image1)

**Fig 1:** Ellipsometry analysis: (a) Ellipsometry Parameters psi (\(\Psi\)) and delta (\(\Delta\)) b) Plots of refractive index and extinction coefficients.

![X-ray photoelectron spectra](image2)

**Fig 2:** X-ray photoelectron spectra (XPS) of Si 2p level indicating the presence of silicon nitride and other phases.

The first two peaks centered at 99.4 and 100 eV were attributed to elemental Si and are spin-orbit doublet, 2p\(_{3/2}\), 2p\(_{1/2}\). The other three peaks centered around at 101.6, 102.6 and 103.6 eV are attributed to Si coordinated in Si\(_3\)N\(_4\), Si\(_2\)O\(_x\)N\(_y\) and SiO\(_2\) networks respectively. It is evident from the Si 2p XPS spectra that the silicon nitride phase is formed along with other phases. Moreover the formation of silicon oxynitride and silicon dioxide can be attributed to the surface oxidation of the as-deposited samples or could be due to the incorporation of residual oxygen. The most important point to be noted is that the excess silicon/Si coordination and contribution of silicon nitride phase increase after thermal treatment, which is a signature of phase stabilization and is consistent with our white light ellipsometry fitting results.

In addition, we have also investigated the possibility of silicon nanocrystals (Si-NC) growth in as-deposited hydrogenated silicon nitride thin films. The formation of Si-NC in as-deposited films is directly confirmed by high resolution transmission electron microscopy and selected area diffraction pattern. We have further explored the room-temperature photoluminescence studies on as-deposited films as a function of flow rate ratio (Fig. 3). This emission can be due to several kinds of
radioactive recombination centers in non-stoichiometric silicon nitride films [8, 9].

Further, one can also see existence of silicon nanocrystals from Raman spectra (fig. 4). From the analysis of Raman spectra it is evident that as-deposited films contain amorphous silicon quantum dots, which could be one of the sources of light emission, apart from structural disorders [10, 11]. However, more detailed studies are in progress to understand the more realistic mechanism for the light emission.

4. CONCLUSIONS

Systematic studies on the hydrogenated amorphous silicon nitride thin films reveals that there is a substantial densification (up to 29% reduction) and large changes in refractive index (up to 22% enhancement) after RTA. Moreover out-diffusion of hydrogen which takes place on RTA is believed to play a key role in the overall structural evolution of the host matrix phase. Present of various structural phases, namely Si–Si coordination, Si3N4, SiO2, and SiOxNy is confirmed by XPS. In addition to this room temperature photoluminescence is also observed in the as-deposited a-SiNₓ:H films. Which could be due to formation of silicon nanocrystals and/or structural disorder. Overall the present study indicates that one can tailor the optical constants and light emission from Si nanostructures embedded in hydrogenated silicon nitride films over a wide range which is desirable for active and passive devices.

REFERENCE
