Tuning the optical properties of RF-PECVD grown μc-Si:H thin films using different hydrogen flow rate

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Abstract

In this paper we study the effect of H₂/SiH₄ dilution ratio (R) on the structural and optical properties of hydrogenated microcrystalline silicon embedded in amorphous matrix thin films. The thin films are prepared using standard RF-PECVD process at substrate temperature of 200 °C. The effect of hydrogen dilution ratio on the optical index of refraction and the absorption coefficient were investigated. It was observed that by incorporating higher hydrogen flow rate in the films with low SiH₄ concentration, the optical index of refraction can be tuned over a broad range of wavelengths due to the variation of crystalline properties of the produced films. By varying the hydrogen flow of μc-Si:H samples, ~8% and 12% reduction in the index of refraction at 400nm and at 1500nm can be achieved, respectively. In addition a 78% reduction in surface roughness is obtained when 60sccm of H₂ is used in the deposition compared to the sample without any H₂ incorporation.

1. Introduction

Developing efficient, low cost, and long term stable materials is very critical for the next generation of electronic and photonic devices. Hydrogenated amorphous silicon (a-Si: H) with its inherently disordered nature has been considered as an essential material for integrated active photonic and photovoltaic devices [1-3]. Hydrogenated amorphous silicon has one order of magnitude higher optical absorption coefficient compared to c-Si [4]. Furthermore, it can be deposited on a low cost substrate due to its low deposition temperature. This gives a high compatibility with most CMOS based semiconductor technology. However, a-Si:H exhibits a light-induced degradation called a Steabler-Wronski effect (SWE) [5], which results in degradation of solar cells efficiency. In addition, the poor conductivity of a-Si:H and the complexity of doping mechanism compared to c-Si call for further investigation and improvement in growth parameters [6].

In the last decade, transition from amorphous to microcrystalline and nano-crystalline embedded on amorphous silicon matrix has been observed by modifying the deposition condition using RF-PECVD reactor [7]. It was reported that μc-Si:H exhibits greater stability under radiation compared to a-Si:H, which increases the carrier
mobility and improves the solar cell conversion efficiency \([8,9]\). The growth of nc-Si:H/µc-Si:H thin films using RF-PECVD requires low SiH\(_4\) concentration and high hydrogen content \([10,11]\). Moreover changing other deposition condition like RF power density, Ar dilution and chamber pressure introduce different structural properties of the nc-Si:H/µc-Si:H films \([12,13]\).

In this paper we present a µc-Si:H embedded in amorphous matrix deposited at 200 °C using RF-PECVD rector. The correlation between the dilution ratio of H\(_2\)/SiH\(_4\) and the films structural and optical properties has been studied, with special attention to the impact on the optical index of refraction \([14]\). Furthermore, the correlation between the hydrogen flow rate, grain size and the crystalline density of microcrystalline silicon films in tuning the optical characteristic of a-Si:H has been characterized using Raman spectroscopy and variable angle elipsometry. By varying the hydrogen flow rate in the produced µc-Si:H, the index of refraction can be tuned over broad band of wavelengths spectrum. In the context of these findings, tailoring the optical properties of the produced films is very promising for silicon photonics waveguides, electro-optical modulators, and solar cell application.

2. Experimental Details

Two series of silicon films, A and B, were prepared using standard PECVD system activated by a 13.56MHz RF signal at a substrate temperature of 200°C. The films are deposited on Corning 1737 glass substrate and (100) P-type Si substrate. A mixture of ultrahigh pure SiH\(_4\), H\(_2\), and Ar are used as precursor gases. In all cases the chamber pressure is set at 1000mtor, an Ar flow of 100sccm and a power density of 10W are used. The glass substrates are cleaned by rinsing them in Acetone and then in Isopropanol using ultrasonic cleaner for 20min. After this the samples are rinsed with DI water and dried with nitrogen flow. The Si substrates are cleaned by diluted 1:10 Hydrofluoric acid solution. In series A of deposited films, the saline concentration was varied and the hydrogen flow rate is fixed at 100sccm. However, in series B films, a low saline concentration is used to form the microcrystalline silicon and the hydrogen flow rate was varied from zero to 100sccm. Both series A and B of depositions are summarized in table 1.

The structural characterization of the silicon films was carried out using a High Resolution Scanning Electron Microscopy (HRSEM) and stylus profilometer (Veeco Dektak 150) to verify the film thickness and the deposition rate. Based on the HRSEM cross section, the profilometer step height and the deposition time, the growth rate is estimated to be 47.5nm/min. Raman spectroscopy (Witec Aplha 300-Raman, 532nm wavelength laser, and power
<75mW) is used to study the films vibrational modes and the crystalline fraction volume. Moreover, the surface of the films are analyzed with CSI instrument (AFM Nano-Observer with) atomic force microscopy with a silicon tip (7nm radius of curvature) in the tapping mode.

In order to study the optical quality of the deposited layers, the optical parameters of the microcrystalline layers are extracted using J.A Woolam Variable Angle Ellipsometer and UV/VIS/NIR spectrophotometer.

<table>
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<th>Table 1. Summary conditions for films</th>
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<tr>
<td>Series A</td>
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<td>SiH₄ Flow  (sccm)</td>
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3. Results and Discussion

3.1 Raman analysis

3.1.1 Series A samples

Figure 1 shows the Raman spectra of silicon films deposited at different SiH₄ flow rate and fixed hydrogen flow of 100sccm. The Raman peaks are analyzed by fitting them with Lorentz model. As can be seen in Fig.1, the peak position shifts from 496cm⁻¹ at R=10 (R is the H₂/SiH₄ ratio) to 511cm⁻¹ at R=50. By increasing the SiH₄ concentration (low R) the peaks shift to lower vibrating frequency modes and show a larger FWHM value. The films with high dilution ratio (high R) have vibrational modes closer to the value of the transverse-optic (TO) mode of the crystalline silicon (520cm⁻¹) [15], and lower FWHM values. Therefore, films deposited with higher R tend to be more crystalline than low R films (high SiH₄ concentration).

Transformation from amorphous silicon to polycrystalline is highly temperature dependent process. Elevated temperatures between 600ºC-800ºC are typically used in many fabrication process [16]. As a result, changing the
H$_2$/SiH$_4$ ratio using RF-PECVD provides a possibility to form a hydrogen-induced crystallization of amorphous silicon at very low temperature of 200 °C.

![Fig.1 Raman spectra of series A silicon films](image1)

### 3.1.2 Series B samples

In order to study the hydrogen dilution role in the crystalline fraction of silicon films and their optical proprieties, in series B samples, the hydrogen flow rate was varied from zero to 100sccm at fixed low SiH$_4$ flow of 5sccm. The Raman spectra of series B silicon films are analyzed by deconvolution into three Gaussian peaks corresponding to crystalline, amorphous and micro-crystalline phase [17]. Fig.2 shows the Raman spectra of series B sample with zero hydrogen flow rate. From this figure, we can observe that those films have mixed phases at low SiH$_4$ concentration. Fig.3 depicts the Raman peak of the films deposited at different hydrogen flow and fixed SiH$_4$ of 5sccm.

![Fig.2 Raman spectra of series B silicon film deposited with zero hydrogen flow](image2)
The films deposited with higher $R$ show more peak shift toward crystalline phase, apart from a certain amount of amorphous phase still present. Moreover, the Raman peak that corresponds to the $R=12$ films present a high degree of asymmetry and distortion of amorphous matrix due to the variation of crystalline size and their density.

Figure 4 shows the crystalline fraction as a function of H$_2$ flow rate, clearly samples with high hydrogen flow rate demonstrate a considerable increase in crystallinity (33% at 100sccm) compared to the un-hydrogenated sample (17.2%). Therefore, a sufficient hydrogen content is an essential factor for crystal growth at both low SiH$_4$ concentration and low deposition temperature. The incorporation of hydrogen and the growth kinetics in the deposited films can be explained by different mechanism. One possibility is that hydrogen can penetrate into the film by diffusion and etching the week bonds in the Si-Si network, which promotes the generation of a prolong chain of crystalline order, or by hydrogen attachment to dangling bonds [18].
3.2 AFM surface analysis

The AFM technique is used to correlate the role of the hydrogen flow rate with the surface roughness of the deposited μc-Si:H in series B silicon films. Fig. 5 depicts a 78% reduction in the surface roughness when 60 sccm of H₂ flow is used. However, the sample with 100 H₂ flow shows a higher RMS roughness of 0.48 nm, which can be associated with the growth of facets and upper surfaces of crystallites on the film [19]. This observation matches the Raman spectra taken from this sample where the peak shifts more toward the Silicon crystalline phase. For optical and electrical applications, a smooth film surface is very critical for the reduction of the interface defects in case of heteroepitaxial integration. Moreover, it mitigates the carrier scattering in the surface current devices.

3.3 Optical properties of the Films

The (n, κ) optical values are extracted from spectroscopic ellipsometry using fitting routines. The fitting is performed for 0.3 μm silicon films by considering it as an absorbing layer on top of transparent glass substrate. Fig. 6 shows the effect of changing the SiH₄ flow rate for Series A films on the real part of the optical index of refraction and the optical absorption coefficient. The measurements are performed at a fixed H₂ flow rate of 100 sccm. The refractive index n for all dilution ratios increases for shorter wavelength and reaches a maximum at ~ 415 nm. For wavelengths longer than 415 nm, the curves converge to n~3.5. Samples prepared with R = 5 (i.e less hydrogen dilution) show higher n values than those with R = 50 for wavelength longer than 500 nm. As a result, the volume fraction of μc-Si:H in the R=50 case is higher. This is in a good agreement with reported results.
references [6, 20] as well as with our Raman analysis, where a-Si has higher $n$ values than c-Si for wavelength larger than 500nm. Similarly, the absorption coefficient values for samples with $R = 5$ are higher than those with more hydrogen dilution.

Fig. 6 optical parameters of series A silicon films (a) Index of refraction (b) Absorption coefficient

Fig. 7 shows the optical index of refraction and the absorption coefficient of the silicon samples of series B deposition. Interestingly, the change in the hydrogen flow of $\mu c$-Si:H samples shows ~ 12% reduction in the index of refraction at 400nm and ~ 8% at 1500nm. Therefore, by incorporating more H$_2$ flow during the deposition of $\mu c$-Si:H, the index of refraction can be tuned over a broad range of wavelengths. Moreover, the absorption coefficient is also reduced by 16% at high hydrogen flow. This is in agreement with the Raman spectra where an increase contribution of the crystalline phase for high hydrogen flow in series B films are confirmed.

Fig. 7 optical parameters of series B silicon films (a) Index of refraction (b) Absorption coefficient
4. Conclusion
In summary, the optical properties of a-Si:H films was tuned by adjusting the dilution ration of H$_2$/SiH$_4$. The dilution ratio ($R$) was mainly changed, while other deposition parameters like RF power, chamber pressures, and Ar dilution were kept constant. It was found that, a high hydrogen flow rate during the deposition increases the degree of crystallinity of the produced films. Furthermore, reducing the SiH$_4$ flow rate stimulates the growth of µc-Si:H. The RMS roughness of the µc-Si:H prepared at different H$_2$ flow rate show a 78% reduction when 60sccm of H$_2$ is used in the deposition compared to the sample without any H$_2$ incorporation. The changes in the optical index of refraction and absorption coefficient in the produced µc-Si:H were studied as a function of hydrogen flow rate. It was found that the optical index of refraction of µc-Si:H with different hydrogen flow rate can be tuned by changing the crystalline proprieties of µc-Si:H. This result was achieved at low deposition temperature of 200 °C which is promising for CMOS compatible silicon photonic application.

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References


