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Enhancing The Optical And Electrical Properties of Si-based Nanostructured Materials

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Abstract

Multilayer structures of Si rich silicon oxide (SiO\textsubscript{x}) alternated with two types of dielectric sublayers viz. SiO\textsubscript{2} or SiN\textsubscript{x} have been studied. An enhancement in the density of nanoclusters within the SiO\textsubscript{x} sublayer is achieved by using the reactive magnetron co-sputtering method. The effect of SiN\textsubscript{x} sublayer thickness on the photoluminescence properties is investigated. We succeed in enhancing the absorption and the photoluminescence properties of the multilayers by replacing SiO\textsubscript{2} by SiN\textsubscript{x} sublayers. We also achieve a higher conductivity in SiO\textsubscript{x}/SiN\textsubscript{x} with an improved thermal budget. This preliminary study gives a deep insight to optimize materials for future solar cell device applications with enhanced properties at reduced thermal budget.

Keywords: Si nanoclusters; SiO\textsubscript{x}; SiN\textsubscript{x}; multilayers; absorption; photoluminescence; resistivity.

1. Introduction

Nanostructures of silicon have attracted the photovoltaic field due to their promising optoelectronic properties and their compatibility with the already existing Si technologies. The visible emission from Si based structures is attributed to the quantum confinement of the photogenerated carriers [1,2]. Hence it becomes important to precisely control the size of the nanostructured silicon. A multilayered (ML) configuration of Si nanoclusters (Si-ncs <5nm) alternated with dielectric sublayers such as SiO\textsubscript{2} is proved to exhibit quantum confinement effects [3-6]. An efficient absorption of light by the solar cell can be

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attained by optimizing the density and size of Si-nc in such a ML configuration. The fabrication and optimization of Silicon Rich Silicon Oxide (SiO\textsubscript{x})/SiO\textsubscript{2} MLs using reactive magnetron sputtering approach have been demonstrated in our earlier reports [7,8]. Though an efficient photoluminescence is obtained by the aforesaid MLs the higher bandgap of SiO\textsubscript{2} serves as a barrier for electric transport and in turn the conductivity. Hence the replacement by SiN\textsubscript{x} with smaller bandgap becomes a possible solution for more efficient solar cells. Visible luminescence from Si-nc embedded in SiN\textsubscript{x} matrix has been recently demonstrated [9,10]. However there is no comprehensive study of electrical properties from SiO\textsubscript{x}/SiN\textsubscript{x} MLs. In this paper we propose reactive magnetron co-sputtering growth approach to increase the Si-ncs concentration within the SiO\textsubscript{x} sublayers of MLs. We also compare two types of MLs (I) SiO\textsubscript{x}/SiO\textsubscript{2} and (II) SiO\textsubscript{x}/SiN\textsubscript{x} grown by this approach and analyze their optical and electrical behaviors. This paper reports an enhancement in the optoelectronic properties of SiO\textsubscript{x}/SiN\textsubscript{x} in comparison to SiO\textsubscript{x}/SiO\textsubscript{2} MLs.

2. Experimental

The SiO\textsubscript{x}/SiO\textsubscript{2} (SiO\textsubscript{x}=SiO\textsubscript{2}=3.5) and SiO\textsubscript{x}/SiN\textsubscript{x} (SiO\textsubscript{x}=3.5 and SiN\textsubscript{x}=5.5) multilayers (referred herein to as type (I) and (II) MLs) were deposited on (100) Si substrate at 500°C, by a reactive magnetron cosputtering method. The SiO\textsubscript{x} sublayers were fabricated by simultaneously sputtering the Si and the SiO\textsubscript{2} targets with power densities 7.4 W/cm\textsuperscript{2} and 2.2 W/cm\textsuperscript{2} respectively by adding hydrogen into the Ar plasma. The term “reactive” is used since the process takes advantage of the capability of hydrogen to reduce the oxygen in the plasma from the sputtered target as detailed elsewhere [8]. The SiN\textsubscript{x} sublayers were fabricated by sputtering the Si target while adding nitrogen into the Ar plasma. The SiO\textsubscript{2} thickness and the SiO\textsubscript{x} thickness in both types (I) and (II) of MLs were fixed at 3.5nm. In order to understand the influence of the SiN\textsubscript{x} sublayers, different thicknesses ranging from 1.5 nm to 5.5 nm were investigated for the PL behavior. The SiO\textsubscript{x}/SiO\textsubscript{2} and SiO\textsubscript{x}/SiN\textsubscript{x} MLs were annealed at 1100 °C for 1 hour and 1000 °C for 1 minute respectively under N\textsubscript{2} atmosphere. These annealing treatments were chosen because they were the best for the aforesaid layers in terms of PL properties as reported elsewhere [11]. The spectroscopic ellipsometry analysis was carried out between 1.5 and 4.5 eV by using a Jobin Yvon ellipsometer (UVISEL) at an incidence angle of 66.3° and different parameters such as the thickness, the refractive index n and the extinction coefficient k (imaginary part of the complex index) of the film was obtained. The fitting of the experimental data was performed with DeltaPsi2 software [12] using a dispersion law based on the Forouhi–Bloomer model (FBM) [13] modified for amorphous semiconductor and insulating materials using an improved parameterization [14]. The absorption coefficient \(\alpha\) was calculated as follows: \(\alpha = 4\pi k/\lambda\), where \(\lambda\) is the wavelength of the incident beam. The PL spectra of the annealed samples were obtained using TRIAX 180 Jobin Yvon monochromator in the wavelength range of 550-1100 nm with a R5108 Hamamatsu PM tube and using the 488 nm argon line from an Innova 90C coherent laser as excitation wavelength. EF-TEM was performed on cross-sectional specimen using a TEM-FEG microscope Tecnai F20ST equipped with an energy filter TRIDIEM from Gatan. The energy-filtered images were obtained by inserting an energy-selecting slit in the energy-dispersive plane of the filter at the Si and at the SiO\textsubscript{2} plasmon energy (16 eV and 23 eV respectively) and with a width of approximately 2 eV. Electrical measurements were made by using two probes apparatus (SUSSMicrotec EP4 equipped with Keithley devices) to obtain the I-V characteristics.

3. Results and Discussions

3.1. Structural studies

Fig.1 compares the EF-TEM image of our earlier MLs obtained by sputtering only SiO\textsubscript{2} in hydrogen rich plasma (Method 1) and the MLs discussed in this paper, grown by simultaneous sputtering of SiO\textsubscript{2}
and Si in hydrogen rich plasma (Method 2). In addition to the structural analysis with regard to the growth techniques, to better understand the two types of MLs at their best annealing treatments, we have presented here SiO$_x$/SiO$_2$ grown using Method 1 (Fig. 1a) and SiO$_x$/SiN$_x$ grown using Method 2 (Fig. 1b). An enhancement in the concentration of the Si-ncs ($10^{13}$ nc/cm$^2$) is achieved by using method 2, compared to the one obtained by method 1 ($10^{12}$ nc/cm$^2$). It can also be seen that the Si-ncs in SiO$_x$ obtained by Method 2 have lesser inter-distances in comparison to the SiO$_x$/SiO$_2$ MLs grown using Method 1. The Si-ncs are well distributed throughout the SiO$_x$ layers and there is no formation of Si-ncs in both kinds of dielectric sublayers.

![EF-TEM image obtained at Si plasmon peak (16eV): (a) Method 1 grown SiO$_x$/SiO$_2$ (1100°C, 1h Annealed) [7] and (b) Method 2 grown SiO$_x$/SiN$_x$ (1000°C, 1min Annealed)](image)

### 3.2. Absorption and photoluminescence studies

The extinction coefficient $k$ of refractive index of the MLs, is obtained by fitting experimental ellipsometry data. The absorption coefficient $a$ is then calculated using the following equation:

$$a = (2\omega k)/c$$

where, $\omega$ is the angular frequency of the photon and $c$ is the velocity of light.

The effect of annealing treatments on the absorption coefficient was investigated and Fig. 2a shows the absorption coefficient spectra of ML types (I) and (II) annealed during 1h at 1100°C and 1 min at 1000°C respectively. The newly employed reactive magnetron co-sputtering technique has allowed us to enhance the absorption coefficient from the MLs owing to the high density of Si-ncs achieved and/or the replacement of the SiO$_2$ sublayer by the SiN$_x$ one (Fig. 2a). It can be seen from this figure SiN$_x$ based ML has higher absorption coefficient than SiO$_2$ based ML in the 2.5-5.5eV range. Fig. 2b corresponds to the PL spectra obtained from the MLs in the visible range. The luminescence intensity from the short time annealed SiO$_x$/SiN$_x$ ML is around 1.4 times higher compared to the luminescence obtained from long time annealed SiO$_x$/SiO$_2$ based ML. Also, the modeling [15] of emission in the multilayer structures performed considering the interference effects did not show any inversion of the intensity trends. There is also a shift in the peak position towards the higher energy in the SiO$_x$/SiN$_x$ ML and this is one of the advantageous aspects in terms of solar cell applications. Though the SiN$_x$ sublayer thickness plays a significant role in increasing the emission intensity as can be seen from the inset in Fig. 2b, it is still advantageous as it yields enhanced optical properties. However, the change in the SiN$_x$ sublayer thickness showed only a negligible variation in the PL peak position (around 800 nm) and hence we infer that the Si-ncs sizes remain the same. Though the origin of PL from SiO$_x$/SiN$_x$ and its intensity trends are still under investigations, we infer from our earlier studies that there is a large contribution of Si-ncs in the
light emission, for the following reasons: a) Even if SiN<sub>x</sub> shows a defect related PL, when alternated with SiO<sub>x</sub> sublayers we have shown that the peak position shifts towards lower energies thereby making the luminescence of Si-nc more pronounced [11], b) The EF-TEM image in Fig.1b confirms the formation of Si-nc within the SiO<sub>x</sub> sublayer even after a short time annealing treatment thereby indicating the Si-ncs formed within the ML plays a dominant role in the optical properties even after a short time annealing treatment.

3.3 Electrical studies

I-V characteristic curves of the (I) and (II) MLs with and without annealing are presented in Fig.3a and Fig.3b. In the case of SiO<sub>x</sub>/SiO<sub>2</sub> though an annealing treatment of 1h at 1100°C was successful in producing a significant density of Si-ncs, supported by an increase in the emission properties, this structure offers high resistivity and in turn offers limitations for device applications. The annealed MLs had a lesser conductivity compared to non annealed ones. The MLs resistance and resistivity after annealing were deduced from Fig.3a to be 14500 Ω and 0.73 x 10<sup>8</sup> Ω.cm respectively.

In the case of SiO<sub>x</sub>/SiN<sub>x</sub> a strong increase in the conductivity is noted after the annealing treatment. The values of resistance and resistivity as calculated from the I-V curves shown in Fig.3b are 1753 Ω and 0.14 x 10<sup>7</sup> Ω.cm respectively. The conductivity in SiN<sub>x</sub> based ML is enhanced by more than one order of
magnitude compared to the oxide based ML owing to the reduced band gap of the former. Besides, even in the case of electrical studies, a short time annealing treatment in SiNₓ based ML has proved to be successful in enhancing the conductive properties.

4. Conclusion

Structural and optoelectronic investigations on two types of SiOₓ based MLs have been made. An incorporation of ‘co-sputtering’ in addition to our earlier used reactive magnetron sputtering methods for the fabrication of SiOₓ layers has favoured an increase in the Si-nc density and a uniform distribution throughout the SiOₓ sublayers. The annealing treatment of 1100°C for 1 hour was found to be the best in SiOₓ/SiO₂ MLs and 1000°C for 1 minute in the case of SiOₓ/SiNₓ MLs. The formation of Si-ncs in SiOₓ/SiNₓ MLs after a short time annealing treatment is promising for device applications with a control over the thermal budget. Replacement of SiO₂ by SiNₓ in the ML structures, showed an enhancement in absorption and also in PL emission arising from Si-ncs. In addition to this improvement in optical properties, enhancement in conductivity is also observed in SiOₓ/SiNₓ MLs after a short time thermal annealing in contrast with the poor conductive SiOₓ/SiO₂ MLs which become more resistive with annealing.

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