Materials Letters 203 (2017) 50–53

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Double stack layer structure of SiN_x/pm-Si thin films for downshifting and antireflection properties

E. Mon-Pérez [a], A. Dutt [a], J. Santoyo-Salazar [b], M. Sánchez [c], G. Santana [a,*]

[a] Instituto de Investigaciones en Materiales, UNAM, A.P. 70-360, Coyoacán C.P. 04510, Mexico
[b] Departamento de Física, CINVESTAV-IPN, A. P. 14-740, C. P. 07000 México, Mexico
[c] Facultad de Física, Universidad de La Habana, C.P. 10400, Cuba

ARTICLE INFO

Article history:
Received 5 April 2017
Received in revised form 2 May 2017
Accepted 27 May 2017
Available online 27 May 2017

Keywords:
Chemical vapor deposition
Semiconductors
Luminescence
Nanocrystalline materials
Solar energy materials
Optical materials and properties

ABSTRACT

In this work, we propose a double stack layer design of SiN_x/pm-Si thin films by using dichlorosilane in plasma enhanced chemical vapor deposition (PECVD). Adequate deposition condition has been found to attain the average minimal reflectance corresponding to two different layers of SiN_x and pm-Si at the suitable refractive index and thickness of the respective films. The average reflectance of the structure is reduced to ~3% at normal incidence for a wavelength range from 190 to 1100 nm as in comparison to single layer of SiN_x thin film structure. Furthermore, using transmission electron microscopy (TEM) presence of double layer stack and formation of silicon quantum dots (QD's) in the size regime of 3–4 nm has been found. Photoluminescence (PL) diminishment in the double layer structure as in comparison to the single layer of SiN_x thin film confirms the effective absorption and total internal reflection induced due to the gradient refractive index. However, visible photoluminescence observed in the present work also remarks the downshift property from the thin film which could subsequently improve the efficiency in silicon solar cells. Present work highlights the prospective of novel structure for downshifting, antireflection and as an passivation coating in new generation of silicon solar cells.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

It is well-known fact that the maximum theoretical efficiency upper limit for a single-junction mono crystalline silicon (c-Si) solar cell is around 30% [1]. However, actual photovoltaic device performs well below this reported theoretical value. Reason are the various losses, like optical, recombination and parasitic resistive losses in the solar cells [2]. Among optical losses, there exists subcategories like reflection, recombination and thermalization factors. To reduce reflection loss which constitutes 30% among different mechanisms, one of the most used antireflective coating is SiN_x thin films [3,4]. SiN_x has surplus advantage of simplicity in the fabrication procedure but it suffers from the major drawback of strong dependence on the incidence angle. Solution to this restriction is the recent investigations made on the graded refractive index (GRIN) multilayer thin-film stack, or nanostructured surfaces [5,6]. Additional research has been made on the double-layer thin film stack, which has shown promising results of low reflectance as in response to irradiation [7], and SiN_x/SiO_2 layers [8,9]. Furthermore, fabrication of these layers is less complicated as compared to the earlier mentioned GRIN stack based antireflection coating. Many investigations has been put forward towards the development of SiN_x thin films using PECVD [10,11] because of tunable refractive index; as well, it provides an excellent level of passivation, and high transparency in the visible region due to high band gap [3,4]. However, there exists no report of double-layer with the silicon nitride and polymorphous silicon. In the later sections, it has been demonstrated new scheme for the improvement of antireflection property of solar cells.

Apart from the enormous study made on the antireflection layer to improve the efficiency of solar cells several other investigations has been carried out simultaneously (to reduce thermalization). In current years, lot of study has been done to improve the conversion efficiency of silicon solar cells by employing microstructure and nanostructures [12]. As reported earlier, using nanostructures, new kind of generation of solar cells has been investigated, where, higher energy photons could be absorbed and will be converted to lower energy photons when absorbed by layer containing silicon QDs to exploit the unutilized part of the solar spectrum (downshifting) [13].

In our previous reports, using dichlorosilane, research has been made on the development of polymorphous silicon thin films [14,15]. Advantages of this precursor material is the possibility to

* Corresponding author.
E-mail address: gsantana@iim.unam.mx (G. Santana).

http://dx.doi.org/10.1016/j.matlet.2017.05.121
0167-577X/© 2017 Elsevier B.V. All rights reserved.

produce nanoparticles in the stable as-deposited thin films without annealing treatment.

In the present work, using the existing features of the SiN_x as an antireflection coating, new kind of in-situ grown double-layer structure has been developed with additional deposition of polymorphous layer. Thickness of both of the layers have been controlled in such a way that the minimum reflection has been observed from the thin film structure. Finally, depending on the formation of nanoparticles in both cases, photoluminescence and reflectance characteristics obtained in this work could be used for a good anti-reflection coating, for passivation and as well as for downshifting in silicon-based solar cells structures. Numerous applications with additional feature of cost sustainability could promote the development of thin films proposed in the present work.

2. Experimental

Thin films were deposited by using PECVD reactor operating at RF of 13.56 MHz with parallel plates of 128 cm^2 in area and 1.5 cm apart. Hydrogen-diluted SiH_2Cl_2 gas was used as the silicon precursor. For both pm-Si (SiN_x) layers, the SiH_2Cl_2, Ar and H_2 flow rates were fixed at 15 sccm (10 sccm), 50 sccm (40 sccm) and 100 sccm (20 sccm), respectively, whereas, the substrate temperature, deposition time, the RF plasma power and the deposition pressure were fixed at 200 °C (150 °C), 1 min (2 min 55 s), 100 W (50 W) and 750 mTorr (250 mTorr), respectively for two different layers. However, NH_3 flow rate was kept constant at 10 sccm for the SiN_x layer. The chemical bonding structure of the films was analysed by using a FTIR spectrometer (Nicolet-560) in the range of 400–4000 cm^{-1}. For TEM analysis, samples were observed in a JEOL (JEM-2010) with LaB6 filament and an acceleration voltage of 200 kV. Photoluminescence (PL) was measured using a He-Cd laser (Kimmon Koha Co., Ltd., Centennial, CO, USA) with an excitation wavelength of 325 nm. Filmetrics brand model F10-RT-UV was used for the antireflectance measurement.

3. Results and discussion

Fig. 1(a) shows the representative FTIR spectra of the as-deposited SiN_x thin films and whereas, Fig. 1(b) shows the FTIR of the bilayer presented in this work. In both cases, one strong absorption band that corresponds to the Si-N stretching vibration around at 860 cm^{-1} can be observed.

As can be seen from Fig. 1, hydrogen can be found mainly bonded with nitrogen and silicon species at N-H bending modes at 1180 cm^{-1} (stretching at 3360 cm^{-1}) and Si-H stretching mode near 2220 cm^{-1}. However, profound absorption peaks in case of double layer show the hydrogenation and well passivation of the thin films. Additionally, the presence of the Si-O-Si stretching mode around 1070 cm^{-1} in case of double layer shows the slight oxidation which could occur during the deposition process. Presence of oxidized layer could also be confirmed from the TEM image (Fig. 2).

TEM image displayed in Fig. 2(a) illustrates the presence of bilayer of silicon nitride (~65 nm) partially visible and polymorphous silicon (~29 nm), respectively. As mentioned earlier, presence of oxidized layer (~4 nm) is besides clearly noticeable from the micrograph. Fig 2(b) shows the presence of Si-QD's embedded in the SiN_x matrix. In the inset of Fig. 2(c) selected are electron diffraction (SAED) pattern illustrates the high crystalline nature of the QD́s of silicon in the matrix.

Fig. 3(a) and (b) displays the PL spectra of the as deposited samples. As can be seen, the PL main peak can be found at around 480 nm with a broad peak from around 400–700 nm in both cases (normalized peak in Fig. 3(b) validates that in both cases maximum peak intensity can be found at around 480 nm). The presence of wide distribution of QD's (Fig. 2) could provoke this strong emission by quantum confinement. Hence, it can be illustrated that in the present case thin films exhibited bright and stable emission in the visible region, which further can be used in the shift conversion property in the silicon solar cells to utilize the higher energy part of the solar spectra.

It is interesting to discuss about the diminishing of the PL in the double stack layer case (Fig. 3(a)). Double layers consist of structure with lower refractive index of SiN_x (n = 1.7) in the top side and following with higher refractive index of polymorphous layer (n ~3). As the laser source penetrates in across the structure, it suffers absorption due to higher n and total internal reflection. Whereas, in the case of the single layer, reflection is higher and the reflected signal can be seen in the form of intense PL emission. Although, in case of double layer due to better absorption and ideal antireflection properties, reflected light from the deposited material is almost absorbed and can be seen with weakened PL emission in Fig. 3(a).

Fig. 3(c) and (d) shows the reflectance spectra of the two different types of samples. As can be observed in Fig. 3(c), the sample shown minimum total reflection as similar to the theoretical reflection corresponding to one particular wavelength. Furthermore, in case of double layer (Fig. 3d) improvement in the minimum antireflection property can be observed to ~3% by the adjustment of the refraction index and thickness of the stack structure.

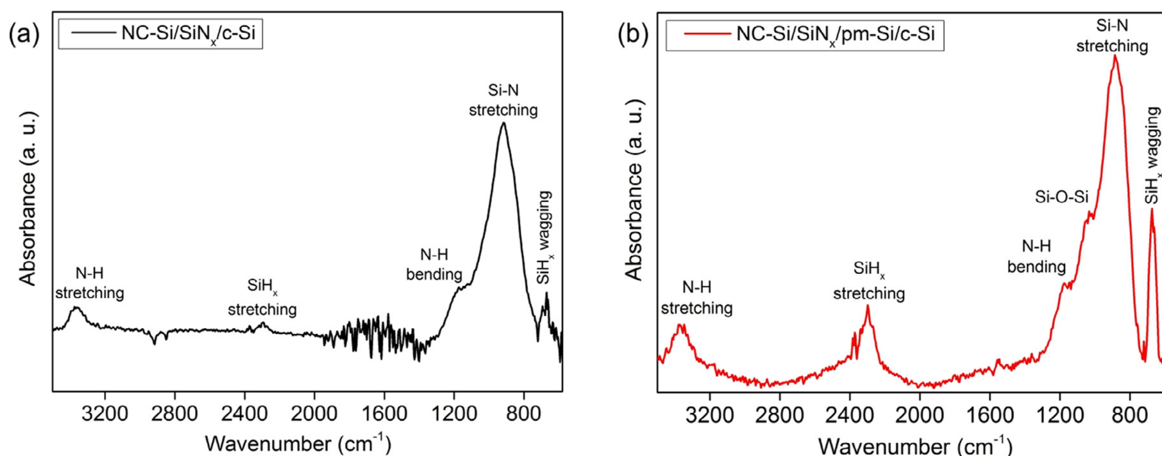

Fig. 1. FTIR spectra of as-deposited thin films (a) single layer (b) double stack layer structure.

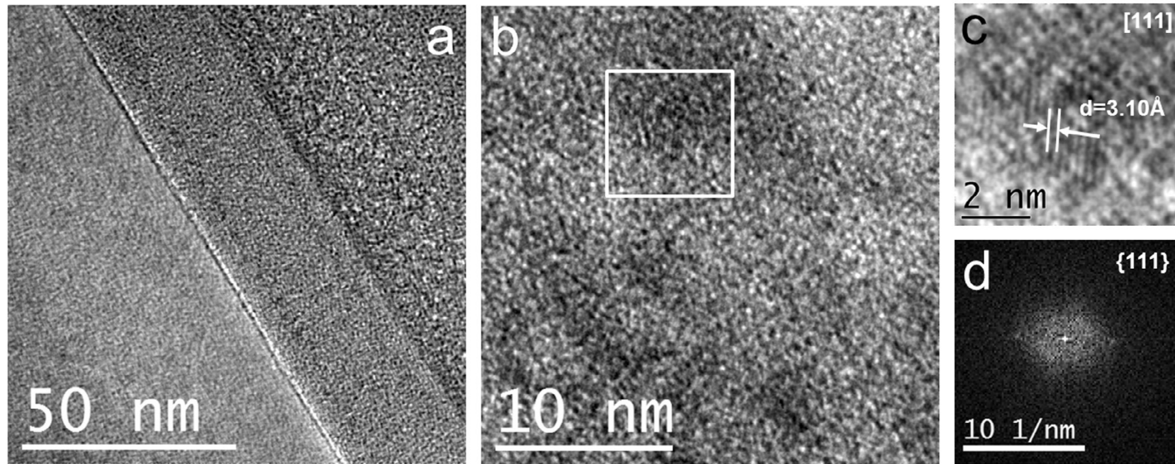

Fig. 2. (a) TEM micrograph of the double layer structure in cross section (b) Si-QD's of 4 nm embedded in the SiN_x matrix c) HRTEM from selected area in (b) and d) FFT with {111} from silicon crystals.

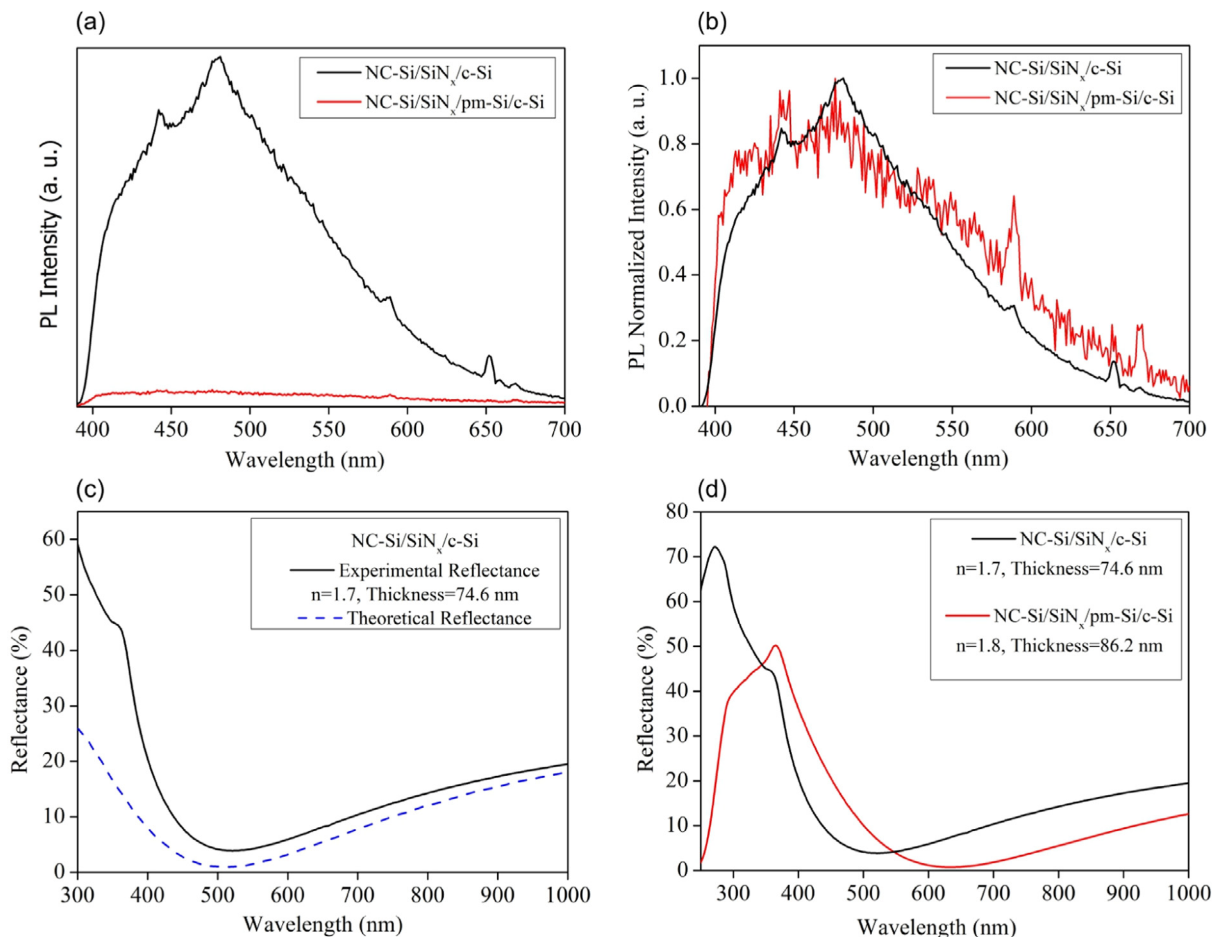

Fig. 3. (a) Visible PL of the as-deposited sample when excited with He-Cd laser at room temperature (b) Normalized PL spectra; (c) Comparison of the reflectance spectra of the single layer sample with the theoretical model (d) Comparison of the reflectance of the single layer with the double stack layer structure.

4. Conclusions

Presence of stack layers of silicon nitride and polymorphous silicon grown using dichlorosilane as a precursor gas by PECVD has been demonstrated. TEM micrographs confirmed the formation of double layer with controlled thickness, which lastly, illustrated the improvement in the minimum reflection as compared to the single layer structure. Even more, deposited thin films shown the intense photoluminescence in the visible region, which remarks the downshift property from this material. To sum up, the double layer structure proposed in the present work could be used as an excellent antireflection coating and downshifting/ passivating layer in silicon solar cells for their efficiency improvement.

Acknowledgements

The authors acknowledge financial support for this project from DGAPA-UNAM PAPIIT Projects IN108215 and IN107017. E. Mon-Pérez is grateful for CONACyT scholarship 517361. We want to thank Josue E. Romero-Ibarra and C. D. Ramos Vilchis for technical assistance.

References

[1] W. Shockley, H.J. Queisser, J. Appl. Phys. 32 (1961) 510–519.
[2] R. De Rose, P. Magnone, M. Zanuccoli, E. Sangiorgi, C. Fiegna, in: 2013 14th Int. Conf. Ultim. Integr. Silicon, 2013, pp. 205–208.
[3] H. Nagel, A.G. Aberle, R. Hezel, Prog. Photovoltaics Res. Appl. 7 (1999) 245–260.
[4] P. Doshi, G.E. Jellison, A. Rohatgi, Appl. Opt. 36 (1997) 7826–7837.
[5] W.H. Southwell, Appl. Opt. 24 (1985) 457.
[6] H. Sankur, W.H. Southwell, Appl. Opt. 23 (1984) 2770.
[7] T. Yang, X. Wang, W. Liu, Y. Shi, F. Yang, Opt. Express 21 (2013) 18207–18215.
[8] K. Choi, K. Kim, J. Cera. Process. Res. 11 (2010) 341–343.
[9] K.P. Lim, D.K.T. Ng, Q. Wang, J. Phys. D. Appl. Phys. 49 (2016) 85302.
[10] M. Bose, D.K. Basa, D.N. Bose, Mater. Lett. 48 (2001) 336–341.
[11] P. O'Brien, E.W. Hill, M.A. Malik, M.J. Toohey, Mater. Lett. 61 (2007) 284–287.
[12] G. Conibeer et al., Thin Solid Films 511–512 (2006) 654–662.
[13] V. Badescu, A. De Vos, A.M. Badescu, A. Szymanska, J. Phys. D Appl. Phys. 40 (2007) 341–352.
[14] B.M. Monroy et al., J. Lumin. 121 (2006) 349–352.
[15] E. Mon-Perez et al., Nanotechnology 27 (2016) 455703.