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Development of n-μc-SiO_x:H as cost effective back reflector and its application to thin film amorphous silicon solar cells

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Abstract

Development of doped silicon oxide based microcrystalline material as a potential candidate for cost-effective and reliable back reflector layer (BRL) for single junction solar cells is discussed in this article. Phosphorus doped μc-SiO_x:H layers with a refractive index ~2 and with suitable electrical properties were fabricated by radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) technique, using the conventional capacitively coupled reactors. Optoelectronic properties of these layers were controlled by varying the oxygen content within the film. The performance of these layers as BRL have been investigated by incorporating them in a single junction amorphous silicon solar cell and compared with the conventional ZnO:Al based reflector layer. Single junction thin film a-Si solar cells with efficiency ~9.12% have been successfully demonstrated by using doped SiO:H based material as a back reflector. It is found that the oxide based back reflector shows analogous performance to that of conventional ZnO:Al BRL layer. The main advantage with this technology is that, it can avoid the ex-situ deposition of ZnO:Al, by using doped μc-SiO:H based material grown in the same reactor and with the same process gases as used for thin-film silicon solar cells.

Keywords: PECVD; Amorphous silicon; Thin film; Solar cells; Back reflector layer

1. Introduction

Thin film silicon solar cells using amorphous silicon (a-Si:H) as absorbers has fascinated the scientific community for last several decades, owing to their flexibility in engineering the optical gap, inexpensive raw materials with low processing temperature, and the ability to manufacture on large area substrates/on a large scale However, a-Si:H material exhibits a metastable light-induced degradation of its optoelectronic properties, called as the Staebler–Wronski effect (Staebler and Wronski, 1977), which can be minimized by reducing the thickness of the absorber layer in the a-Si:H cell. A thinner absorber layer produces less current, hence lesser conversion efficiency for the solar cell. In order to overcome this issue various light-trapping schemes are employed. The most commonly used technique is the introduction of a back reflector layer (BRL) with suitable refractive index and conductivity between the cell and the back metal contact, which allows achieving longer light paths in the absorbing film, which in turn increases the light absorbing capability of thinner active layers. In the conventional p-i-n cell configuration, ZnO:Al is widely used as BRL which significantly improves the solar cell performance, predominantly in the long wavelength region (Dagamseh et al., 2008; Guozhen et al., 2009; Hüpkes

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et al., 2008; Banerjee and Guha, 1991). Nevertheless, in view of industrial scale manufacturing, the main drawbacks of ZnO-based BRL include its high material, and capital equipment cost for the additional ex situ deposition process.

Phosphorus doped hydrogenated silicon oxide (SiO_x:H) has been widely investigated for various photovoltaic applications due to its unique electrical and optical properties, which can be modulated over a wide range by varying the deposition conditions. Its potential as a BRL as well as an intermediate reflector layer (IRL) for thin film silicon based solar cells has been investigated by many research groups (Yamamoto et al., 2006; Buehlmann et al., 2007; Das et al., 2008). Silicon oxide material (SiO_x:H) is known to have a two-phase structure, in which the Si:H part contributes to the conductivity whereas the SiO part provides the optical gap. As the optical gap is high, the layer will absorb less light, resulting in enhancement of the short circuit current in a thin single junction a-Si solar cell (Buehlmann et al., 2007). Other advantages of SiO_x:H include: lower material cost for large scale production, and the material can be developed utilizing the same equipment used for depositing the solar cell layers, thereby reducing the overall process complexity.

In this paper, the use of seeding technique for developing high quality doped SiO_x:H films with suitable optoelectronic property is discussed (Watanabe et al., 1993). Ultrathin undoped μc-SiO_x:H seed layer films have been developed and optimized, followed by the deposition of n-type μc-SiO_x:H films by the conventional radio frequency plasma enhanced chemical vapor deposition (RF-PECVD) method. The n-μc-SiO_x:H films thus grown were applied to single junction a-Si solar cells by replacing the conventional ZnO:Al BRL and their performance was evaluated.

2. Experimental

The undoped μc-SiO_x:H seed layers and n-type μc-SiO_x:H films were prepared in one chamber of a conventional capacitively coupled multichamber PECVD reactor developed indigenously (base vacuum ~10^{-9} Torr) employing 13.56 MHz RF excitation source (Seren IPS, USA). The properties of these oxide layers were optimized by varying CO_2, SiH_4, PH_3 and H_2 flow ratio as well as RF power and process pressure. The thickness of these films were measured using stylus profiler (Veeco Dektak 6 M). The optical E_{04} values as well as the refractive index were estimated from the transmission spectra measured by using a spectrophotometer (PerkinElmer, lambda 750). The electrical properties of the oxide films were investigated by co-planar conductivity measurements (Keithley 6487) using evaporated aluminum electrodes with 12 mm length and a separation of 3 mm gap. The oxygen content in the film and the bonding configuration was studied by FTIR (Shimadzu IRA) spectroscopy and the crystalline volume fraction of the film was calculated by micro Raman spectroscopy (LabRAM HR-laser wavelength 514 nm and power 5 mW). The structural properties of these films are studied by high resolution transmission electron microscopy (JEOL JSM-2010).

Single junction oxide based p-i-n solar cells (area 1 cm^2) with structure; Glass/SnO_2:F/p-a-SiO_x:H/i-a-SiO_x:H(buffer)/i-a-Si:H/n-a-SiO_x:H/i-μc-SiO_x:H(seed)/n-μc-SiO_x:H(BRL)/Al were prepared using the optimized oxide based BRL. These solar cells have been characterized by measuring the current–voltage characteristics under STC (AM1.5G, 25 °C and 1000 W/m^2) and the external quantum efficiency (EQE) (Spectranova SN Series). A comparative study of performance of solar cells with similar structure were carried out, with the conventional ZnO:Al based BRL and the in situ developed n-μc-SiO:H material. Optimized process recipe was used to fabricate mini modules of size 30 cm × 30 cm on TCO (SnO_2:F) coated glass substrate. Triple laser scribing technique was adopted for monolithic integration of the mini module by using 1064 and 532 nm wavelength laser beams. The current–voltage characteristics of the mini solar modules prepared were measured by using a pulse type solar simulator (Spectranova SN series).

3. Result and discussion

In order to develop n-μc-SiO_x:H based BRL suitable for the thin film amorphous silicon solar cell application, it is necessary that the material should have a lower refractive index and lower absorbance in the near-IR region. However, a very low refractive index may lead to poor electrical properties which may in turn lead to inferior solar cell properties. The most critical aspects to optimize the material properties include the precise controlling of the process parameters like, the hydrogen dilution ratio (SiH_4/H_2) and the carbon dioxide addition ratio (CO_2/SiH_4). Earlier work by Watanabe et al. (1993) and Banerjee et al. (2002) show that the incorporation of an intrinsic seed layer (μc-SiO_x:H) can enhance the growth of n-μc-SiO_x:H layers with very promising properties for a BRL. Hence, in the present work, the BRL have been developed using the seeding technique. The optimized process parameters for the deposition of seed layer and n-μc-SiO_x:H back reflector are given in Table 1.

The structural properties of the n-μc-SiO_x:H films were investigated by high resolution transmission electron microscopy (HRTEM). Fig. 1(a) shows the HRTEM micrograph of n-μc-SiO_x:H film, having a thickness of 750 Å grown on seed layer of thickness 55 Å, and Fig. 1(b) shows the micrograph of a n-μc-SiO_x:H film of 800 Å thickness deposited without any seed layer.

The TEM micrograph of doped oxide layers grown with seed layer, as shown in Fig. 1(a), indicates the presence of a mixture, composed of nanocrystal clusters embedded in a amorphous matrix, with a typical crystallite feature size >5 nm. The influence of seed layers, on the growth of microcrystallinity in n-μc-SiO_x:H film is clear from the micrographs. It is observed that n-μc-SiO_x:H films grown

Table 1
The optimized deposition parameters for growing the seed layer and n-μc-SiO:H back reflector layer with substrate temperature: 220 °C.

Type of layer	SiH_4/H_2	CO_2/SiH_4	PH_3 (sccm)	Pressure (Torr)	Power density (mW/cm^2)
Seed layer	1:70	0.6	–	1.5	20
n-μc-SiO:H	1:80	1.2	0.2	1.5	20

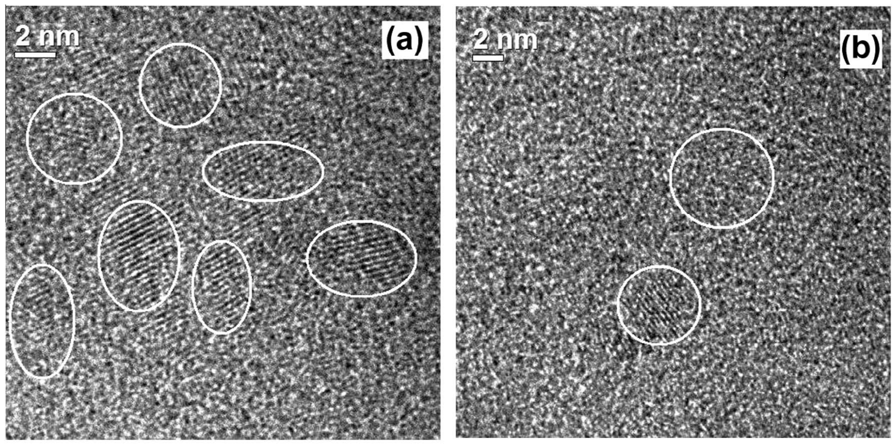

Fig. 1. High Resolution Transmission electron micrograph of (a) n-μc-SiO:H film on μc-SiO:H seed layer and (b) n-μc-SiO:H film deposited without seed layer.

on μc-SiO_x:H seed layers is of better-quality than that of the films grown without the seed layer, Fig. 1(b). The TEM images portrays the importance of seed layer in enhancing the microcrystallinity of n-μc-SiO_x:H film.

The optical absorption spectrum of n-μc-SiO_x:H films were taken under ambient conditions and is shown in Fig. 2. Optical E_{04} values for these films were estimated from the curve as ~2.27 eV.

Refractive index of the n-μc-SiO_x:H material was calculated in different ways to confirm the exact value. Three different routes were used: reflection measurement (Siqueiros et al., 1988), Swanepoel's method (Shaaban et al., 2012) and ellipsometric measurement. Using reflection and Swanepoel's method, the refractive index value obtained was ~2.1 at 600 nm. This is in good agreement with the value of refractive index obtained from ellipsometry measurements as shown in Fig. 3. The conductivity measurements of n-μc-SiO_x:H films were studied by co-planar method, which showed dark conductivity (σ_D) of about 10^{-4} S/cm.

The crystalline volume fractions (X_c), which is defined as the ratio of the integrated area of the microcrystalline peak at 520 cm^{-1} to the total peak area, of n-μc-SiO_x:H films grown with, and without the seed layer were calculated

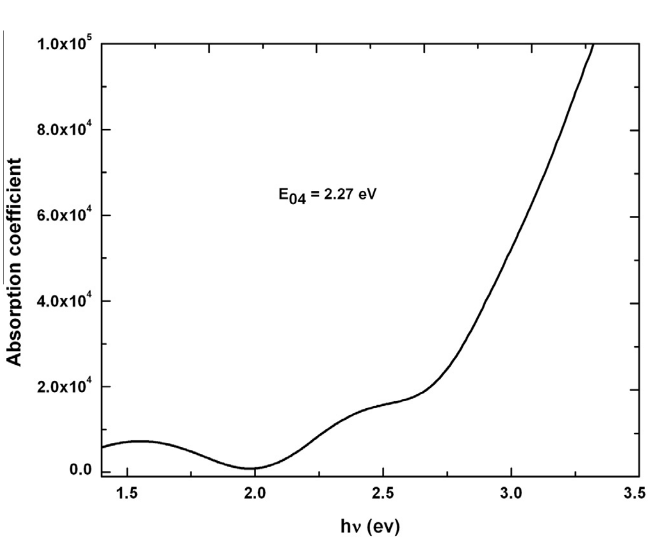

Fig. 2. Variation of absorption coefficient with energy for n-μc-SiO:H material.

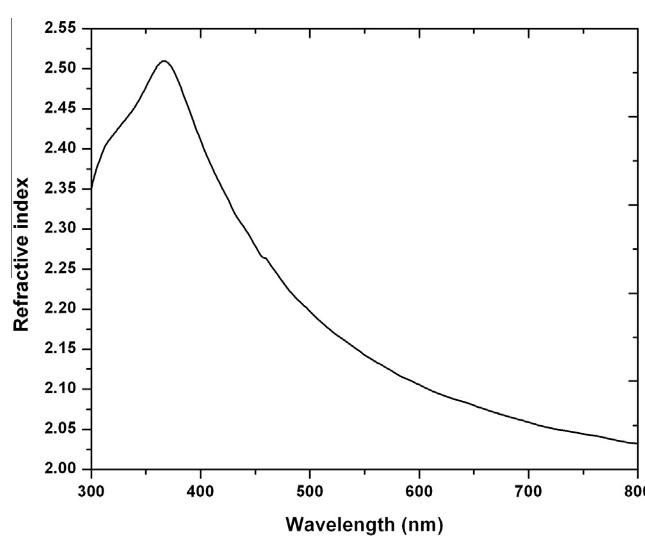

Fig. 3. Variation of refractive index of n-μc-SiO:H material with wavelength.

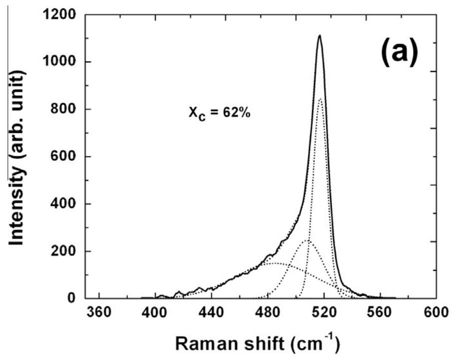

Fig. 4. Raman spectra of n-μc-SiO:H film deposited on (a) undoped μc-SiO:H seed layer of 55 Å thickness and (b) without any seed layer.

from Raman spectra and are shown in Fig. 4(a) and (b), respectively.

Raman spectroscopy analysis reveals the presence of a mixture of μc-Si:H and amorphous silicon oxide (a-SiO_x) phases. The crystalline volume fraction of the n-μc-SiO_x:H film grown using μc-SiO_x:H seed layer is greater than that of the film without any seed layer. It is thought that the oxygen-rich amorphous phase leads to a low refractive index and high band gap, while the μc-Si:H phase contributes to achieving a sufficient dark conductivity (Buehlmann et al., 2007; Grundler et al., 2010).

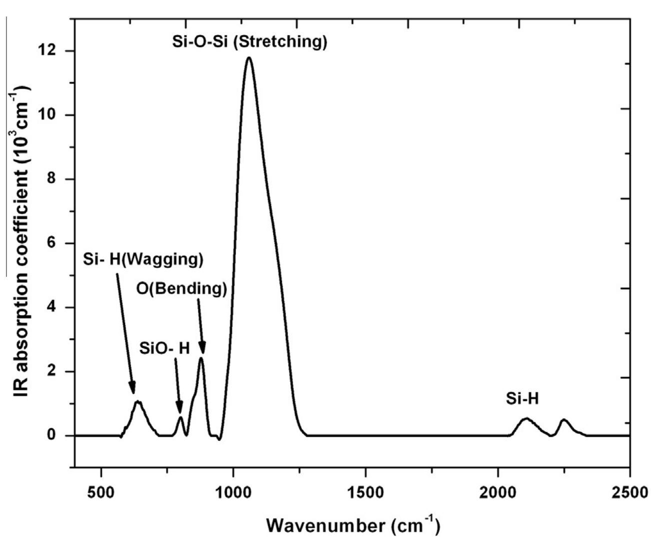

Fig. 5. Full range IR absorption spectra of n-μc-SiO:H films deposited on Si wafer.

The FTIR spectrum of the oxide material is shown in Fig. 5 and it was used to determine the oxygen content in the films as well as to study the bonding configuration. Atomic percent of oxygen C(O) Lucovsky et al., 1983 incorporated in the film is obtained from the integrated absorption strength of IR absorption in the range of 900–1200 cm^{-1} (Cuony et al., 2011), and it is found to be 34%.

The effect of the n-μc-SiO_x:H reflector materials on the solar cell performance, was evaluated by incorporating these layers in single junction a-Si solar cells. The performance of oxide based back reflector solar cell were compared with solar cells with conventional ZnO:Al back reflector. The total thickness of the BRL was maintained at ∼800 Å. Table 2 shows the optimized process conditions used for the fabrication of single junction a-Si solar cell with n-μc-SiO_x:H back reflector layer.

It is observed that similar performance can be obtained by using the optimized n-μc-SiO_x:H layer as the back reflector instead of the conventionally used ZnO:Al. Comparison of the IV and EQE curves are given in Fig. 6(a) and (b) respectively. A marginal improvement of the open circuit voltage (V_{oc}) as well as short circuit current (I_{sc}) has been observed for cells grown using n-μc-SiO_x:H back reflector, in comparison with ZnO:Al reflector. This could be due to the marginal improvement in spectral response of the cells with the n-μc-SiO_x:H BRL (Veneri et al., 2010).

The optimized process parameters developed in small area cells were used for fabricating mini modules of size 30 cm × 30 cm having 27 cells. The highest initial efficiency obtained for the mini modules with oxide based back-reflector is 8.0%. The module IV parameters obtained

Table 2
The optimized single junction a-Si solar cell process condition with n-μc-SiO:H reflector layer.

Type of layer	SiH_4/H_2	B_2H_6 (sccm)	CO_2/SiH_4 (sccm)	PH_3 (sccm)	Power density (mW/cm^2)	Pressure (Torr)	Thickness (Å)
p-a-SiO:H	1:17	0.1	1.17	–	21	1	250
i-a-SiO:H (buffer)	1:25	–	0.2	–	21	1	70
i-a-Si:H	1:1.3	–	–	–	21	1	2500
n-a-SiO:H	1:1.7	–	0.13	0.6	14	1	250
i-μc-SiO:H (seed)	1:70	–	0.6	–	20	1.5	55
n-μc-SiO:H (BRL)	1:80	–	1.2	0.2	20	1.5	750

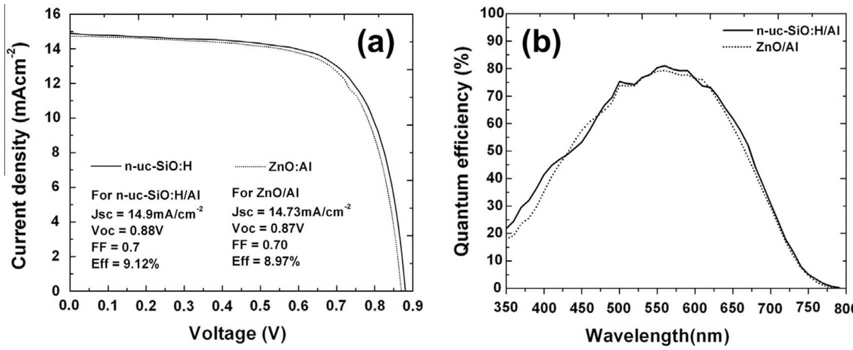

Fig. 6. Comparison of (a) IV curve and (b) EQE curve of the single junction a-Si solar cells with different types of back reflector layers.

are: I_{sc} – 347 mA, V_{oc} – 23.615 V, Fil Factor –64.5%, and P_{max} – 5.3 W. Light induced degradation of these mini modules were studied for 1000 h and it is found that efficiency has decreased to 7.2%, after light soaking. Degradation was found to be only 13% (17% for ZnO:Al based back reflector), because the absorber layer thickness was kept very low (2500 Å) and short circuit current was compensated by the n-μc-SiO_x:H BRL.

4. Conclusion

Silicon oxide (n-μc-SiO_x:H) based BRL, for thin film silicon solar cells, has been successfully developed using seeding technique with lower refractive index and lower absorption at near IR region. HRTEM and Raman spectra investigations hint that the n-μc-SiO_x:H material composed of an amorphous SiO_x:H matrix in which the nanocrystalline Si crystallites are embedded. The optimized n-μc-SiO_x:-H material with required refractive ~2 and electronic conductivity ~10^{-4} S/cm was applied as a back reflector for single junction a-Si solar cells. Comparable performance were obtained for the solar cells fabricated with the conventional ZnO:Al based BRL as well as the doped oxide based material. Result of this study proves that the n-μc-SiO:H material can be used as a substitute for the conventional ZnO:Al based BRL for single junction and as intermediate reflectors in the case of tandem solar cells. From a manufacturing point of view, this can lead to twin advantages: the ability to fabricate the complete solar cell structure (excluding metallization) without breaking vacuum in same PECVD reactor, and also lead to considerable reduction in cost as well as process complexity by eliminating the ZnO:Al BRL.

References

Banerjee, A., Guha, S., 1991. Study of back reflectors for amorphous silicon alloy solar cell application. J. Appl. Phys. 69, 1030.

Banerjee, C., Sarker, A., Barua, A.K., 2002. Reduction of thickness of N-type microcrystalline hydrogenated silicon oxide film using different types of seed layer. Jpn. J. Appl. Phys. 41, L 787.

Buehlmann, P., Bailat, J., Dominé, D., Billet, A., Meillaud, F., Feltrin, A., Ballif, C., 2007. In situ silicon oxide based intermediate reflector for thin-film silicon micromorph solar cells. Appl. Phys. Lett. 91, 143505.

Cuony, P., Duncan, T.L, Alexander, Linus Löfgren, Krumrey, M., Marending, M., Despeisse, M., Ballif, C., 2011. Oxygen-bonding environments in glow-discharge-deposited amorphous silicon-hydrogen alloy films. Mater. Res. Soc. Symp. Proc. vol. 1321.

Dagamseh, A.M.K., Vet, B., Tichelaar, F.D., Sutta, P., Zeman, M., 2008. ZnO:Al films prepared by rf magnetron sputtering applied as back reflectors in thin-film silicon solar cells. Thin Solid Films 516, 7844.

Das, C., Lambertz, A., Huepkes, J., Reetz, W., Finger, F., 2008. A constructive combination of antireflection and intermediate-reflector layers for a-Si/μc-Si thin film solar cels. Appl. Phys. Lett. 92, 053509.

Grundler, T., Lambertz, A., Finger, F., 2010. Phys. Status. Solidi. C7, 1085.

Guozhen, Y., Sivec, L., Owens, j.M., Yan, B., Yang, J., Guha, S., 2009. Optimization of back reflector for high efficiency hydrogenated nanocrystalline silicon solar cells. Appl. Phys. Lett. 95, 263501.

Hüpkes, J., Wätjen, T., Van Aubel, R., Schmitz, R., Reetz, W., Gordijn, A., 2008. Proceedings of the 23rd European PVSEC (Valencia, Spain), p 2419.

Lucovsky, G., Yang, J., Chao, S.S., Tyler, J.E., Czubatyj, W., 1983. Phys. Rev. B 28, 3225.

Shaaban, E.R., Yahia, I.S., El-Metwally, E.G., Al-Azahar, 2012. Validity of swanepoel's method for calculating the optical constants of thick films. Acta Phys. Pol. A 121, 628.

Siqueiros, J.M., Luis Regalado, E., Machorro, R., 1988. Determination of the optical constants of MgF2 and ZnS from spectrophotometric measurements and the classical oscillator method. Appl. Opt. 27, 2549.

Staebler, D.L., Wronski, C.R., 1977. Reversible conductivity changes in discharge-produced amorphous Si. Appl. Phys. Lett. 31, 292.

Veneri, P.D., Mercaldo, L.V., Usatii, I., 2010. Silicon oxide based n-doped layer for improved performance of thin film silicon solar cells. Appl. Phys. Lett. 97, 023512.

Watanabe, H., Haga, K., Lohner, T., 1993. Structure of high-photosensitivity silicon-oxygen alloy films. J. Non-Cryst. Solids 161–166, 1085.

Yamamoto, K., Nakajima, A., Yoshimi, M., 2006. Conf. Rec. of IEEE 4th W. Conf. on Ph. En. Conv. vol. 2, p. 1489.