JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 14, No. 11- 12, November – December 2012, p. 929 - 934

Optimization of wide angle $MgF_2/ZnS/Al_2O_3$ passivation and antireflection film for silicon solar cells

WANG LISHENG*, CHEN FENGXIANG
Department of Physics science and technology, Wuhan University of Technology, China

Preparation of antireflection film is very important for improving the conversion efficiency of solar cells. In this paper, the $MgF_2/ZnS/Al_2O_3$ antireflective coating is optimized on the basis of multilayer antireflection coatings theory. In the optimization processes, the influences of the optimal angle, the angles range of incident sunlight, the spectral response of silicon and the distribution of solar spectrum are also included. And the weighted average reflectivity F was used as a standard to evaluate the quality of the antireflection system. Then the results of the $MgF_2/ZnS/Al_2O_3$ system were compared with that of the $MgF_2/ZnS/SiO_2$ system. The computation results show that 30° is the best angle for designing the antireflection coating system and the Al_2O_3 film can reduce the reflection more effectively than the SiO_2 film. The optimal parameters of wide-angle $MgF_2/ZnS/Al_2O_3$ system are $n_{MgF_2} = 1.38$, $d_{MgF_2} = 119nm$, $n_{ZnS} = 2.40$, $d_{ZnS} = 53nm$, $n_{Al_2O_3} = 1.90$, $d_{Al_2O_3} = 10nm$.

(Received May 31, 2012; accepted October 30, 2012)

Keywords: Solar cells; Antireflection film; Weighted average reflectivity; Wide-angle

1. Introduction

The basic principle of the antireflection is due to destructive interference between the front and back surface of the antireflection film. Research and experimental results show that the reflectivity of solar cell coated with single-layer antireflection coating can be reduced to below 10%, while the reflectivity of solar cell coated with multi-layer antireflection coating can be reduced even lower [1,2]. For solar cells, the commonly used antireflection film materials are MgF_2, SiO_2, Al_2O_3, SiO, SiN_x, TiO_2, Ta_2O_5, ZnS, SnO_2 and ITO, etc [2-4]. The preparation methods are chemical vapor deposition (CVD), plasma enhanced chemical vapor deposition (PECVD), spray pyrolysis, sputtering, evaporation, sol-gel method and so on. These methods were used to deposit different single layer, double-layer and even triple-layer anti-reflection films [5,6]. Among these different antireflection films, everyone has its own advantages and disadvantages. For example, the TiO_2 film has the properties of high refractive index, easy to adjust, simple process, and is more appropriate as antireflection coating. But the TiO_2 film can't passivate the silicon surface, so the open circuit voltage of solar cell with TiO_2 film is low, which will affect the conversion efficiency [7,8]. The SiN_x antireflective coatings have good antireflection and passivation effect, so in commercial production, majority of solar cells were coated with SiN_x film as antireflection film. But compared with TiO_2, the SiN_x film is higher production cost and higher reflection rates after package [9,10]. In addition to the SiN_x film, the SiO_2 film and Al_2O_3 film can also play passivation role on the silicon surface [11,12]. Jan Benick reported that after the deposition of the negative-charge dielectric Al_2O_3 layer, the efficiency of cell reaches to 23.2%, open circuit voltage is 703.6mV, saturation current is $29fA/cm^2$ [12]. Experimental results also show that for the p-Si surface, Al_2O_3 layer have a significant effect of surface passivation even after annealing at moderate temperatures [13].

MgF_2/ZnS double-layer coating is also commonly used antireflection film. The MgF_2 film has a low refractive index (n=1.38) and good thermal stability, with high transmittance in the 120-8000nm wavelength range[14,15]. The refractive index of ZnS is 2.3-2.4, with good mechanical properties and good optical properties, has been the popular selected materials in optical system, especially in the infrared device [16]. MgF_2/ZnS double-layer antireflection film has a perfect antireflection effect compared with other antireflection films. In 1998, the first crystalline silicon solar cell with 24% high efficiency was reported by Martin Green group in University of New South Wales with antireflection coating is MgF_2/ZnS [17]. But MgF_2/ZnS double-layer antireflection film does not have any surface passivation effect, so SiO_2 layer was selected by some research team as passivation layer and the $MgF_2/ZnS/SiO_2$ antireflection and passivation film was proposed [3]. Because the refractive index of SiO_2 is very low (n = 1.46), the reflectivity of $MgF_2/ZnS/SiO_2$ coatings is poor in the short wavelength region. In order to improve the antireflection effect in short wavelength range, SiO_2 was replaced by Al_2O_3 film and $MgF_2/ZnS/Al_2O_3$ passivation and antireflection film was presented.

Until now many authors have reported their optimal antireflection film design of solar cells. Although they have gained good agreements between theoretical calculations and experimental results, while in their design, only normal incident beam is considered as an ideal situation. And in practical applications, generally solar cells and arrays were installed and fixed in a certain direction according to the local longitude and latitude except the concentrator solar cells. In a cycle of the rising and the falling of the sun, the antireflection coating is not always perpendicular to the incident light. At that time it is an oblique incidence with changing incident angle. When the antireflection coating designed under normal incidence was applied to the oblique incidence, the reflective properties changed greatly due to the polarization effect [18]. Therefore, now the $MgF_2/ZnS/Al_2O_3$ system is re-optimized and used to fulfill the daylong needs when the oblique incidence is also considered.

2. Theoretical analysis

The antireflection film is a kind of optical films. For single-layer coating, the reflectivity can be obtained by using Fresnel formula; for the multilayer system, an equivalent interface can be constructed. The reflectivity relies on the equivalent admittance Y. The calculation processed is as the following [19]:

For m layers coating system, the refractive index and thickness of each membrane material are known as $n_k, d_k (k = 1, 2, ...m)$, respectively. The refractive index of incident medium and the substrate material are n_0, n_{m+1}, respectively. The light incident angle is θ_0. η_k is the optical admittance. The interference matrix for the k-layer is:

$$M_k = \begin{bmatrix} \cos\delta_k & i(\sin\delta_k)/\eta_k \\ i\eta_k \sin\delta_k & \cos\delta_k \end{bmatrix} \quad (1)$$

where $\delta_k = 2\pi n_k d_k \cos\theta_k / \lambda \quad (k = 0,1...m)$ is the phase thickness of the k-layer.

Then the interference matrix for the whole m layers system is:

$$M = \prod_{k=1}^{m} M_k \quad (2)$$

In the case of oblique incidence, the admittance values of s polarization and p polarization are different. For the k layer, they are:

$$\eta_k = \begin{cases} n_k / \cos\theta_k & p \text{ component} \\ n_k \cos\theta_k & s \text{ component} \end{cases} \quad (3)$$

Where θ_k can be given by the Snell law,

$$n_0 \sin\theta_0 = n_k \sin\theta_k, k = 1, 2....m, m+1 \quad (4)$$

The expression $Y = C/B$ is the admittance for combinations of multi-layer coatings and the substrate, and B, C were determined by:

$$\begin{bmatrix} B \\ C \end{bmatrix} = M \begin{bmatrix} 1 \\ \eta_{m+1} \end{bmatrix} \quad (5)$$

Where η_{m+1} is the admittance of the substrate layer. The energy reflectivity R of the thin film system is:

$$R = \left| \frac{1 - Y/\eta_0}{1 + Y/\eta_0} \right|^2 \quad (6)$$

For the R_s component , the Y, η_0 values in above expression should be replaced by Y_s, η_{0s}. For the R_p component, the corresponding Y, η_0 should be substituted by Y_p, η_{0p}. The total energy reflectivity R is:

$$R = \frac{R_s + R_p}{2} \quad (7)$$

The reflectivity R of the whole system depends on the structural parameters of each layer. Since the spectral response of silicon ranges from 300 to 1200nm, so only incident light in the 300-1200nm wavelength range is considered. Taking into account the inconsistent between the solar spectrum and the spectral response curve of silicon, the evaluation function is chosen as:

$$F = \frac{\int_{0.3}^{1.2} S(\lambda) SR(\lambda) R(\lambda) d\lambda}{\int_{0.3}^{1.2} S(\lambda) SR(\lambda) d\lambda} \quad (8)$$

where $S(\lambda), SR(\lambda)$ and $R(\lambda)$ represent the spectral distribution of the sun, the spectral response of silicon and the reflectivity of the antireflection coating in the specific wavelength, respectively. So the weighted average reflectivity can be calculated within the entire solar spectrum.

3. Results and discussion

In order to reduce light reflection on surface of silicon solar cells, the simplest approach is coated with a low refractive index film at the surface. Single-layer antireflection coating generally will achieve the V-shape antireflection effect, which means that a lower antireflection effect can be achieved only in certain wavelength, and it is difficult to achieve the desired antireflection effect in the whole spectral range. Multi-layer coating can achieve very good antireflection results, but in the actual production of solar cells, taking into account the cost factors such as materials, technology and so on, the number of antireflection layers is no more than three. While double-layer system such as MgF_2/ZnS antireflection has no any surface passivation effect. So in order to passivate the silicon surface, firstly Al_2O_3 layer can be deposited by atomic layer deposition method, then MgF_2/ZnS antireflection coating was prepared, this coatings system has good antireflection and passivation effect. In this paper, optimization of $MgF_2/ZnS/Al_2O_3$ antireflective coating was presented, as shown in Fig.1. In this system the refractive index of MgF_2 is relatively fixed, usually is selected at 1.38; and the refractive index of ZnS varies in the range between 2.3-2.4; the refractive index of Al_2O_3 is in the range 1.8-1.9.

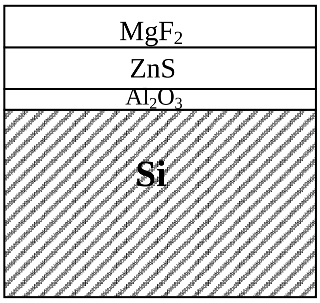


Fig.1 The structure of silicon solar cell.

The goal of optimization the $MgF_2/ZnS/Al_2O_3$ system is to seek the appropriate coating parameters (such as n, d) to ensure that the reflectivity change smoothly in the 300-1200nm wavelength range. Meanwhile the weighted average reflectivity should be as small as possible within the entire solar spectrum. So in practice, the output of the entire PV module is relatively stable even with the incident angle changes, and this is beneficial for the design of PV array. For the incident illumination, the incident angles range from 0° to 60° is considered. If angle is beyond this range, it means that in this time the sun had just risen or is about to fall. The light intensity at that time is not very strong, overtaking the antireflection effect in large-angle will affect the antireflection effect in the time of strong intensity; while if only the small incident angle or normal incidence was considered, the antireflection coating designed for this case can't play a good antireflection effect in daylong application.

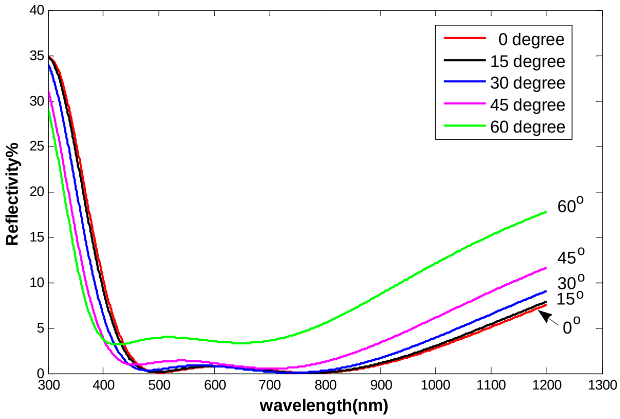


Fig.2 The variation of the reflectivity of optimal antireflection coating on the incident angles and wavelength in the case of optimized for 0°.

Fig.2 shows the optimization results for the $MgF_2/ZnS/Al_2O_3$ system under normal incidence. The thickness of passivation layer is $d_{Al_2O_3} = 10nm$, the refractive index of MgF_2 is 1.38. The other parameters are $d_{MgF_2} = 111nm$, $d_{ZnS} = 51nm$, $n_{ZnS} = 2.4$, $n_{Al_2O_3} = 1.9$. It can be seen from Fig.2 that for normal incidence, the reflectivity of solar cell is relatively low except in 300-400nm wavelength. With the incident angle increases, especially when incident angle increases to 60°, the reflectivity increases rapidly especially in the long-wavelength range, and the reflectivity exceeds over 15%.

In above discussion, the optimal parameters for $MgF_2/ZnS/Al_2O_3$ passivation and antireflection film under normal incidence were discussed, with the presupposition that the Al_2O_3 thickness is 10nm. To study the influence of the thickness of Al_2O_3 passivation layer on the weighted average reflectance F, next the optimal results for different thicknesses of the Al_2O_3 passivation layers under normal incidence were considered.

Fig. 3 shows the variation of the F with the incident angle under different thickness of the Al_2O_3 passivation layer. It can be seen from Fig.3 that the values of F is lower for 5nm and 10nm thick Al_2O_3 passivation layer. Taking into account the 5nm thickness is difficult to realize in practice, so 10nm thick Al_2O_3 passivation layer is used in optimal $MgF_2/ZnS/Al_2O_3$ system.

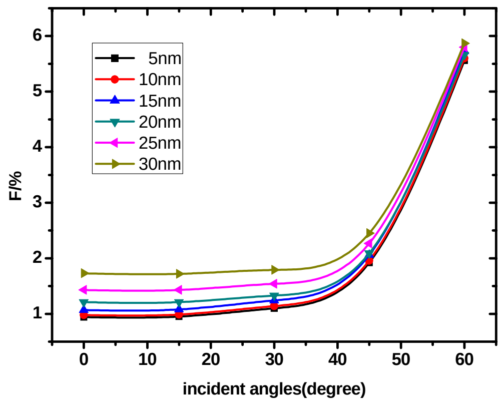
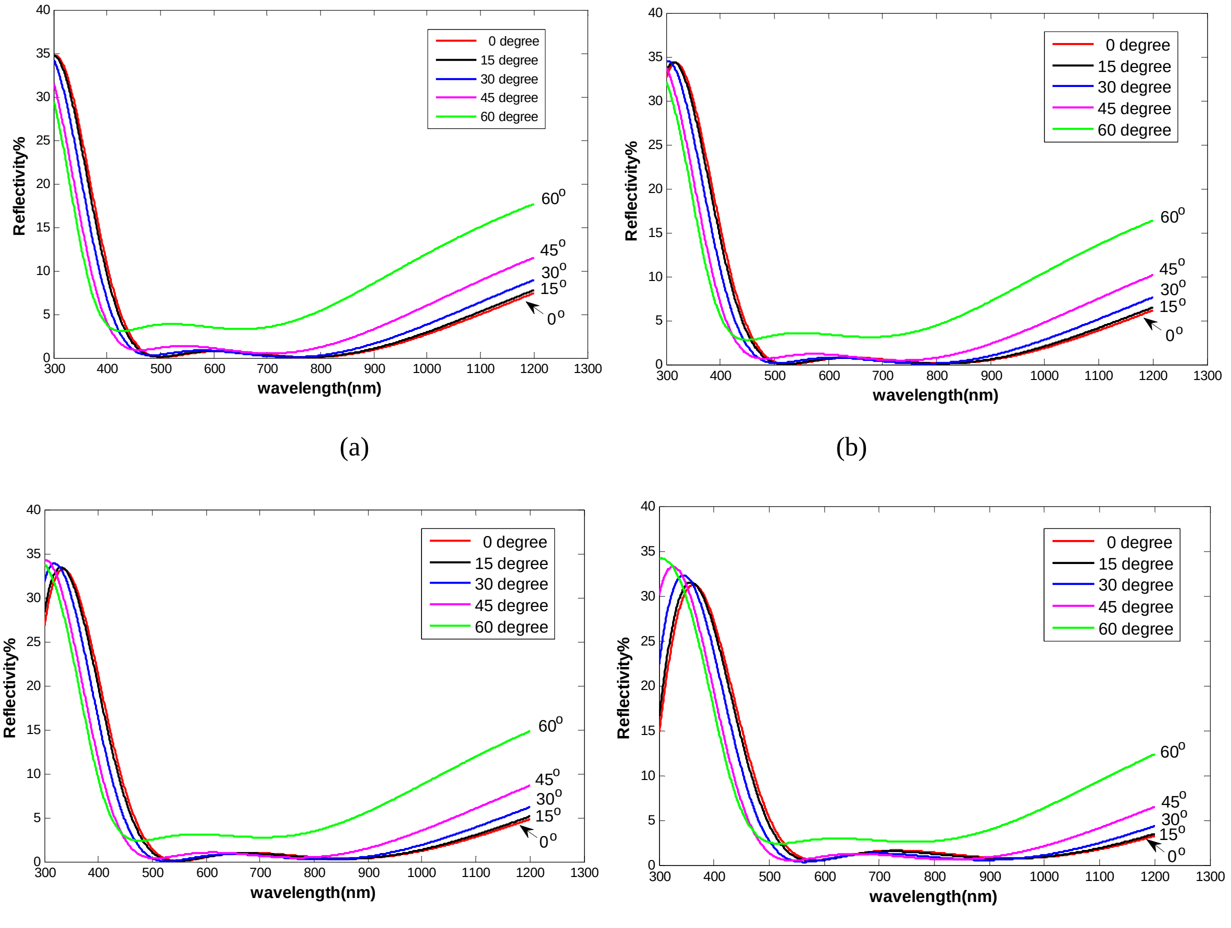


Fig.3 The weighted average reflectance of antireflection coating versus different incident angles and the different thickness of Al_2O_3 passivation layer under the optimization of 0°.

Fig.4 (a) shows the variation of the reflectivity of $MgF_2/ZnS/Al_2O_3$ system with the different incident angles and wavelength under the condition that 15° is selected as the optimized angle, and (b), (c), (d) give the similar results when 30°, 45° and 60° were selected as the optimized angle, respectively. From Fig.4, we can see that the results of 15° are similar with those of 0°. And the reflectivity under different incident angles is always higher in the 300-400nm wavelength; when the sunlight incident angle is large, the higher reflectivity happened in the long wavelength band. Compared the results of 0° and 60° , we found that in the 60° angle case, the long-wavelength reflectivity can be significantly reduced to 10%, but the reflectivity increased in the range 350-450nm wavelength inevitably, which will restrain the absorption of the high-energy photons.



(a) (b)

(c) (d)

Fig.4 Under different optimized angles , the reflectivities of optimal antireflection coating vary with the incident angles and wavelength. The optimized angles equals to (a)15° ;(b) 30° ;(c) 45° ;(d) 60°.

The $MgF_2/ZnS/Al_2O_3$ system optimized in 30^0 angle shows good antireflection properties. When the incident angle is in the range from 0° to 45°, the reflectivity curve changes relatively stable except in the 300-400nm wavelength range; even for the 60° incident angle, the reflectivity remained lower than 15% in most of wavelength band except near 350nm wavelength and 1150nm wavelength. The optimal parameters for $MgF_2/ZnS/Al_2O_3$ antireflection coating are: $d_{MgF_2}=119nm$, $n_{MgF_2}=1.38$, $d_{ZnS}=53nm$, $n_{ZnS}=2.4$, $n_{Al_2O_3}=1.9$, $d_{Al_2O_3}=10nm$. The results for 45° are similar with those of 60°. The reflectivity is only low for the large-angle illumination, but is high in the 350-450nm short-wavelength.

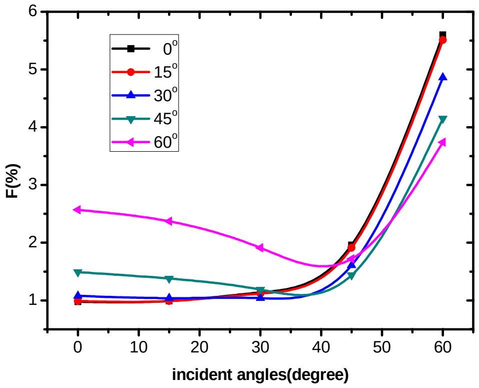


Fig.5 The weighted average reflectance of antireflection coatings versus different incident angles under the optimization of different angles.

In order to compare the impact of the optimized angle on the reflectivity, the intensity distribution in the solar spectrum and spectral response of silicon solar cells were further considered. Fig. 5 shows the weighted average reflectivity F of the antireflection system varies with the incident angle in the whole solar spectrum. As can be seen from Fig.5, if 0° or 15° were used as the optimal incident angle, the F is only low for small incident angle, while F increases rapidly with the incident angle increases; and if 45° or 60° were selected as the optimal incident angle, the F is relatively low in the large angle, while F is higher in the small incident angle compared with other angles. Especially for the 60° case, the F value is nearly 1.5 percentages higher than that of 0° in small incident angle region. These mean that if the antireflective coating was optimized by the larger angle, it can’t play a good antireflection effect in the small incident angle. It is obvious from Fig. 5 that 30° is the optimal angle.

In order to contrast the antireflection effect of the $MgF_2/ZnS/Al_2O_3$ system and the $MgF_2/ZnS/SiO_2$ system, the $MgF_2/ZnS/SiO_2$ passivation and antireflection coating was also designed. In this system, the 10nm-thick SiO_2 passivation layer is considered, where the refractive index of SiO_2 is 1.46. The optimal angle is 30° , the other parameters are: $d_{MgF_2}=119nm$, $n_{MgF_2}=1.38$, $d_{ZnS}=51nm$, $n_{ZnS}=2.4$. Fig.6 shows the variation of the reflectivity of the $MgF_2/ZnS/SiO_2$ system with different incident angles and wavelengths.

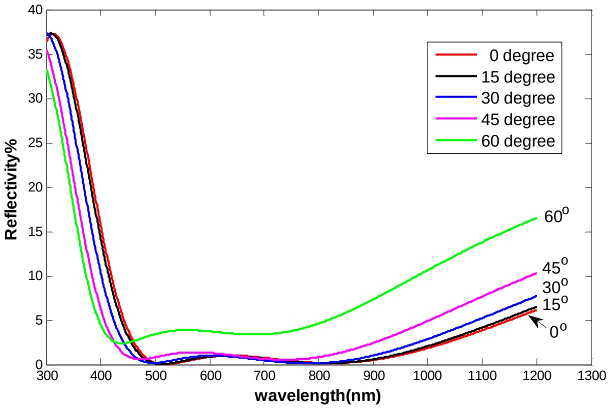


Fig.6 The variation of the reflectivity of optimal $MgF_2/ZnS/SiO_2$ passivation and antireflection coating on the incident angles and wavelength in the case of optimized for 30°.

Comparing the results shown in Fig.6 and Fig. 4 (b), we find that both two systems conform to the same rules. In other words, under the same incident angle, the relationship between the reflectivity and the wavelength for the $MgF_2/ZnS/ SiO_2$ system is similar to that for the $MgF_2/ZnS/Al_2O_3$ system. But in the 300-350nm range, the $MgF_2/ZnS/SiO_2$ system has the higher reflectivity than the $MgF_2/ZnS/Al_2O_3$ system. Table 1 listed the F values for two systems under different incident angles. As can be seen from Table 1, even under the same incident angle, the weighted average reflectivity F of the $MgF_2/ZnS/SiO_2$ system is higher than that of the $MgF_2/ZnS/Al_2O_3$ system. So if the SiO_2 layer is replaced by the Al_2O_3 layer, the antireflection effect of the whole system will be enhanced.

Table 1 The comparison of the weighted average reflectivity F for the $MgF_2/ZnS/Al_2O_3$ system and the $MgF_2/ZnS/SiO_2$ system under the optimal angle 30°

F(%)	0^0	15^0	30^0	45^0	60^0
$MgF_2/ZnS/Al_2O_3$	1.08	1.04	1.04	1.61	4.86
$MgF_2/ZnS/SiO_2$	1.15	1.10	1.10	1.69	5.03

4. Conclusion

In this paper, a wide angle $MgF_2/ZnS/Al_2O_3$ passivation and antireflection coating of silicon solar cell was designed on the basis of the multilayer antireflection coatings theory. The reflectivity of the antireflection system under different optimized angle was also considered. We find that 30° is the optimal angle corresponding to 0-60° incident range. At this time the coating parameters are: $n_{MgF_2} = 1.38$, $d_{MgF_2} = 119nm$, $n_{ZnS} = 2.4$, $d_{ZnS} = 53nm$, $n_{Al_2O_3} = 1.9$, $d_{Al_2O_3} = 10nm$. By comparing the antireflection effect of the MgF_2 / ZnS/Al_2O_3 system with the $MgF_2/ZnS/SiO_2$ system, we find that if the low refractive index SiO_2 film is replaced by the Al_2O_3 layer, the antireflection effect will be better in the whole solar spectrum.

Acknowledgements

This paper is supported by “The Fundamental Research Funds for the Central Universities (Project number: 2011-Ia-002, 2012-Ia-031)”.

References

[1] Wan Gang, Ye Dejun, Cui Rongqiang, Journal of Shanghai Jiaotong University, **32**(12), 21 (1998).
[2] Wang Jianqiang, “The Passivation & Antireflection Property Investigation of PECVD SiNx” [D]. Master thesis of Shanghai Jiaotong University, 2008, pp.16–40.
[3] Sun Xiu-Ju, Li Hai-Ling, Li Xu-Dong, Ren Bing-Yan, Zhou Chun-Lan, Zhao Lei, Wang Wen-jing. Journal of Synthetic Crystals. **38**(3), 547 (2009).
[4] Zheng Zhengrong, Gu Peifu, Chen Haixing, Tao Zhanhui, Ai Manlin, Zhang Meijiao, Tang Jinfa. Acta Optica Sinica., **29**(7), 2026 (2009).
[5] Zhang Li-Jiang, Xiong Bing, Wang Jian, Sun Chang-Zheng, Qian Ke-Yuan, Luo Yi. Semiconductor Optoelectonics., **25**(5), 380 (2004).
[6] Xiao Yi-Qun, Shen Jun, Yao Lan-Fang, Wang Shan, Yang Fan. High Power Laser and Particle Beams. **16**(10), 1281 (2004).
[7] Wong David C, Waugh Art. 24th IEEE Photovoltaic Specialists Conference[C], Hswaii, USA, 1994, 905-908.
[8] Nagel Henning, Aberle Armin G, Hezel Rudolf. Progress in Photovolatics., **7**, 245 (1999).
[9] M. J. Kerr, J. Schmidt, A. Cuevas, J . Appl Phys,, **89,** 3821 (2001).
[10] Schmidt Jan, Kerr Mark. Solar Energy Materials & Solar Cells., **65**, 585 (2001).
[11] Yu Yuebo, Meng Fanying, Guo Qunchao, Jiang Minlin, Hu Yu. Acta Energiae Solaris Sinica. **30**(11), 1465 (2009).
[12] Benick, Jan Hoex, Bram van de Sanden, M. C. M. Kessels, W. M. M. Schultz, Oliver Glunz, Stefan W. Applied Physics Letters. **92** (25), 253504 (2008).
[13] Jan Benick, Armin Richter, Martin Hermle, Stefan W. Glunz. Physica Status Solidi (RRL) – Rapid Research Letters., 3(7-8): 233 (2009).
[14] L. Yu Journal of Quantum Electronics **21**(1), 48 (2004).
[15] S H. Shi, Hefei University of Technology Journal (Natural Science Edition), **26**(3), 384 (2003).
[16] X J. Su, Optical Instruments, **23**(5-6), 68 (2001).
[17] G. C. Zhang, J. H. Zhao, Solar Energy Materials and Solar Cells., **51**, 393 (1998).
[18] Chen Fengxiang, Wang Lisheng. Acta Energiae Solaris Sinica, **29**(10), 1262 (2008).
[19] Lin Yongchang, Lu Weiqiang. National Defence Industry Press. 1990, 35-39.

---

[*] Corresponding author: wang_lesson@yahoo.com.cn