Influence of annealing conditions on tripe-layer TiO$_2$/Si$_3$N$_4$/SiO$_2$ antireflection coatings for GaAs solar cells

Liyu Wu$^{1,2,*}$, Xiaoqiang Li$^{1,2,*}$

$^1$ School of Automotive and Mechanical Engineering, South China University of Technology, 510640, Guangzhou, P. R. China
$^2$ National Engineering Research Center for Near-Net-Shape for Metallic Materials, South China University of Technology, 510640, Guangzhou, P. R. China

$^{*}$wuly2018@qq.com, $^{*}$Lixq@scut.edu.cn

Abstract. In this work, TiO$_2$/SiO$_2$/Si$_3$N$_4$ triple-layer antireflection coatings (TLARC) were prepared on GaAs substrate by RF sputtering and Plasma Enhanced Chemical Vapor Deposition (PECVD). Influence of annealing conditions on the structure and optical properties of TLARC were also investigated. The structure and optical proprieties were analyzed by Grazing Incidence Angle X-ray Diffraction (GIXRD) Fourier Transform Infrared Spectroscopy (FT-IR), Atomic Force Microscopy and UV-VIS spectroscopy. The experimental results were summarized as follows: diffraction peaks of SiO$_2$, Si$_3$N$_4$ and TiO$_2$ respectively appeared in the as-deposited status, and after annealing, new diffraction peak at 25.2° corresponds to TiO$_2$ was confirmed by checking out PDF cards; Stretching vibration of Ti=O, Si-O-Si and N-Si-N was confirmed by FT-IR spectrum; The average reflectance of the TLARC after annealing at 750 ℃ and holding for 5 min reached the lowest value, which was approximately 7.84 %.

1. Introduction

Due to the advantages of large light absorption coefficient, strong radiation resistance and high conversion efficiency, GaAs-based multi-junction solar cells (GBMJSCs) have been mostly used for space and highly concentrated terrestrial application like solar panel. In 1988, dual-junction Al$_{0.37}$Ga$_{0.63}$As/GaAs solar cells has reached an AM0 efficiency of 23 % and AM1.5 efficiency of 27.6 % (0.5cm$^2$) [1]. Triple junction GaInP/Ga(In)As/GaAs solar cells prepared by substrate stripping technology with an AM0 efficiency of 29.7 % have also been reported [2]. Up to now, the energy conversion efficiencies of three-junction solar cells have been steadily increasing year-to-year and achieved the highest conversion efficiency of 30.2 % [3, 4].

In recent years, numerous studies have been carried out, which aiming at reducing the reflection loss of multi-junction solar cells. Currently, the most widely used is to deposit antireflection coatings (ARCs) on the surface of the solar cell to minimize light reflection. Most of the work reported on the ARCs focus on solar cells are just single or double layer coatings for narrow spectrum. Xiao et al. [5] designed and prepared TiO$_2$/SiO$_2$ double-layer antireflection coatings for GaAs multi-junction solar cells, and analyzed the influence of the thickness of TiO$_2$/SiO$_2$ double-layer coatings by programming. The results show that the optimal physical film thickness of SiO$_2$ and TiO$_2$ is 78.61 nm and 50.87 nm respectively by programming technology analysis, additionally, the minimum reflectivity at the short wave center wavelength $\lambda_1$=450 nm is 0.0034 %, the minimum reflectivity at the center wavelength $\lambda_2$=750 nm is 0.495 %. Sung-Mok Jung et al. [6] obtained a ZnS-MgF$_2$ composite dielectric coating by co-sputtering...
ZnS and MgF₂ targets as interlayer, and prepared ZnS/ZnS-MgF₂/MgF₂ three-layer antireflection coatings on a GaAs substrate, which realizes absorption of broadband sunlight in a wide range of incident angles.

Little attention seems that have been paid to optimizing the influence of optical properties of ARCs after heat treatment which prepared on triple junction solar cells. In this paper, we mainly analyzes the effect of the annealing temperature on the performance of the TiO₂/SiO₂/Si₃N₄ triple-layer antireflection coatings (TLARC) prepared on GaAs substrate. Firstly, the thickness of TLARC were simulated via The Essential Macleod (TFC) software. After deposition, the thermal annealing of TLARC was investigated, and its effect on structure and optical properties were also explored.

2. Materials and methods
The optimum refractive index for the layers including the ARCs and ARC’s material, are on the basis of principles of quarter-wave films [7]. For a triple-layer ARC, the optimum refractive index of the gradient layers are as follow:

\[
\begin{align*}
    n_1 &= \frac{1}{2}n_0n_s \quad (1) \\
    n_2 &= \frac{1}{2}n_0n_s \quad (2) \\
    n_3 &= \frac{1}{2}n_0n_s \quad (3)
\end{align*}
\]

where \( n_1, n_2 \) and \( n_3 \) are the optimum refractive index for the top, middle, and bottom layers of the triple-layer coating, respectively. Using \( n_s \) as GaAs substrate and \( n_0 \) as air, in most cases, \( n_0=\text{air} \approx 1.0 \). According to series of published design results, Willey [8] summarizes and proposes a useful empirical formula to estimate the lowest average reflectance as follow:

\[
R_{ave}(B,L,T,D) = (4.378/D)(1/T)^{0.5} \cdot \exp(B-1.4) \cdot \frac{L-1}{(L-1)^{0.5}}
\]  \hspace{1cm} (4)

where \( B \) is bandwidth, definite as \( \lambda_{\text{max}}/\lambda_{\text{min}} \). \( D \) is Difference of high and low refractive index except top layer, definite as \( n_{\text{high}} - n_{\text{low}} \). \( T \) is total optical thickness of antireflection coatings, \( L \) is refractive index of the top layer.

Base on these formula above and consider other factors, materials vary from different layers are taken as follow: SiO₂ [9] (top layer, \( n=1.528 \)), Si₃N₄ [10] (middle layer, \( n=2.176 \)) and TiO₂ [11] (bottom layer, \( n=2.593 \)) for the TLARC. The refractive index (n) and extinction coefficients (k) for GaAs substrate are measured by spectroscopic ellipsometry.

3. Experimental procedure
In this work, prior to the deposition, the substrate (GaAs wafer, 2 inches) were ultrasonically cleaned by acetone, isopropyl alcohol, absolute ethanol and deionized water sequentially for 5 minutes. The samples were deposited by RF Sputtering from a TiO₂ target (99.9% pure) at room temperature and Plasma Enhanced Chemical Vapor Deposition (PECVD) for Si₃N₄/SiO₂ double layers, process parameters of PECVD were shown in Table 1. Post-fabrication annealing was performed in a Rapid Thermal Annealing System (RTP, CT150M) and vacuum sintering furnace (HP-12×12×12) respectively with atmosphere of nitrogen, and the annealing process is illustrated in Table 2. Physical thickness of TLARC were summarized in Fig.1.
The optical properties of the TLARC were measured by UV-VIS spectroscopy (Lambda 900) at the range of 300~1400 nm. Atomic Force Microscopy (AFM, Dimension Edge, Bruke) was used for characterizing the morphology and surface roughness of the films, and for each sample, two different areas were measured for reliability. The structure of the film samples was analyzed by Grazing Incidence Angle X-ray Diffraction (GIXRD) with Cu Kα radiation and Fourier Transform Infrared Spectroscopy (FT-IR, Thermo Nicolet IS10).

Table 1 Process parameters of PECVD.

|          | N_2 /sccm | N_2O /sccm | %SiH_4/N_2 /sccm | NH_3 /sccm | Pressure /mTorr | RF power /W | Temperature /°C |
|----------|-----------|------------|-------------------|------------|-----------------|-------------|----------------|-----------------|
| SiO_2    | 400       | 1000       | 400               | -          | 850             | 50          | 250            |
| Si_3N_4  | 800       | -          | 300               | 12         | 850             | 50          | 250            |

Table 2 Annealing process of TLARC.

| Annealing temperature /°C | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
|--------------------------|----------|----------|----------|----------|----------|
| As-deposited              |          | 500      | 750      | 500      | 750      |
| Time /min                | -        | 5        | 5        | 60       | 60       |

4. Results and discussion

To explore the effect of annealing treatment on the TLARC deposited on GaAs substrate, GIXRD pattern of TLARC prepared under different annealing conditions were characterized in Fig. 2 (a). As it shown in Fig. 2 (a), diffraction peaks of SiO_2 located at 2θ = 53.2° and TiO_2 located at 2θ = 52.2°, 53.8° respectively appear in the as-deposited status, in addition, peak of Si_3N_4 could not be found which illustrated Si_3N_4 are amorphous. All diffraction peaks can be index and no impurity peaks can be identified. Note that after annealing, new diffraction peak at 25.2° corresponds to TiO_2 [12] is confirmed by checking out PDF cards. When the annealing temperature is 500 °C, the peak intensity of SiO_2 and Si_3N_4 reach highest value at 5 minutes, and increasingly gradually broader at 60 minutes, indicating that the Grain size grow up sharply and then refine gradually. As annealing temperature reaches 750 °C, only TiO_2 peak exists while SiO_2 peak disappear, illustrating SiO_2 are amorphous currently. Fig. 2 (b) shows the FT-IR spectrum curve of TLARC annealed at different temperature. In this work, the spectrum curve is used to investigate the vibration state of different functional groups. As shown in Fig. 2 (b), spectral region of 520 cm^{-1} corresponds primarily to the stretching vibrations of Ti=O [13, 14]. The symmetric stretching vibration of Si-O-Si is identified at 1018 cm^{-1}, which is demonstrated by Ferraro J R and Thomas L C et.al [14-18]. Spectral region of 1207 cm^{-1} is associated with stretching vibration of N-Si-N [13, 14, 16, 18], Slight shifting of N-Si-N stretching vibration can be observed obviously, which
probably influenced by the intermolecular forces. The results confirm that the compositions of TLARC are TiO$_2$/SiO$_2$/Si$_3$N$_4$.

Fig. 2 GIXRD pattern (a) and FT-IR pattern (b) of TLARC annealed at different conditions

![GIXRD pattern and FT-IR pattern](image)

Fig. 3 (a), (b), (c), (d) and (e) show the surface morphologies of TLARC deposited on GaAs substrate annealed at different conditions, carried out by AFM with tapping mode. The measurement results of the sample roughness annealed at different conditions in the experiment are shown in Fig. 3 (e). Three-dimensional (3D) AFM images of surfaces in the scan area of 1×1 μm$^2$ with resolution of 512×512 pixels are represented. With the increase in annealing temperature, the surface morphology of films becomes smooth. Compared with deposited film, the particle size in Fig. 3 (b) and (c) are uniform and tiny, whereas the particles begin to unite by annealing in longer time as shown in Fig. 3 (d) and (e). When the annealing conditions are 750 ℃ and 60 minutes, the surface of film becomes rugged rapidly, however, the roughness value still remains lowest (RMS for 1.13 nm and Ra for 0.9125 nm). As shown in Fig. 3 (f), the Ra values range from 0.9125 to 1.17 nm, and the RMS values increase from 1.13 to 1.515 nm. Surface roughness demonstrate a positive correlation with the improvement of annealing conditions, which can be explained that with the increasing of annealing temperature and time, the atomic mobility and distribution of particles on the surface of the films tend to be uniform. Increasing RMS and Ra definitely cause decrease of reflection due to the increase of roughness and scattering of light [19].
Fig. 3 AFM images and surface roughness curve of TLARC annealed at different conditions (a) as-deposited; (b) 500°C for 5 min; (c) 750°C for 5 min; (d) 500°C for 60 min; (e) 750°C for 60 min;
The optical reflectance spectral curve of TLARC deposited on GaAs substrate from 300 to 1400 nm are characterized in Fig. 4, and the Table 3 lists the reflectance of the samples at 500 nm. As shown in Fig. 4 (a), compared with deposited film (average reflectance for 12.13 %), samples after annealing can effectively reduce reflectance, and average reflectance are 10.85 %, 7.84 %, 8.88 % and 9.09 % respectively. The reason for the change is that oxygen vacancies absorbed in films can be eliminated and absorption rate of the layers is reduced. However, from fig. 2 (e), with the increase of annealing time, massive island structures can be found on the surface of film, which lead to the increase of scattering and result in the increase of average reflectance definitely. In the near infrared range (approximately from 700 to 1300 nm), the trend of the measured reflectance curve of the films is basically consistent with the simulated curve. Oppositely, in the near infrared range (approximately from 300 to 700 nm), certain error can be found between simulated and measured curve, this mainly caused by film thickness and homogeneity error due to the process of deposition [20]. Additionally, noise peak appears in the spectral curve due to the factor of grating switching at 850 ~ 900 nm.

![Optical reflectance spectral curve (a) and average reflectance comparison (b) of TLARC annealed at different conditions](image)

Table 3 Reflectance of the different samples at 500 nm.

| Sample | Reflectance /% |
|--------|----------------|
| 1      | 6.54           |
| 2      | 4.29           |
| 3      | 3.21           |
| 4      | 4.70           |
| 5      | 3.77           |

5. Summary
(1) According to results of XRD and FT-IR patterns, TiO$_2$/SiO$_2$/Si$_3$N$_4$ triple-layer antireflection coatings (TLARC) were successfully prepared on GaAs substrate.
(2) Surface roughness demonstrated a positive correlation with the improvement of annealing conditions, the Ra values ranged from 0.9125 to 1.17 nm, and the RMS values increased from 1.13 to 1.515 nm.
(3) The average reflectance of the as-deposited TLARC was 12.13 %. As the annealing temperature increased, the average reflectance of the TLARC gradually decreased and increased with the increase of annealing holding time. The average reflectance of the TLARC after annealing at 750 °C and holding for 5 min reached the lowest, which was 7.84 %.

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