Study of SiNₓ based antireflection coating for GaP/Si heterojunction solar cells

E V Anokhina¹, A V Uvarov² and A S Gudovskikh¹,²
¹Department of Photonics, St. Petersburg Electrotechnical University (“LETI 197376 St. Petersburg, Russia
²St. Petersburg Academic University of RAS, 194021 St. Petersburg, Russia

Abstract. This paper presents the results of a research of the optical properties of SiNₓ layers with various compositions obtained by plasma-enhanced chemical vapor deposition (PECVD). The growth rate and optical properties of SiNₓ obtained using SiH₄ and N₂ at low temperature were determined. A strong dependence of the optical properties of SiNₓ on concentration of silane in the gas mixture during deposition was demonstrated. Antireflection coatings for GaP/Si solar cells were fabricated based on developed SiNₓ layer.

1. Introduction
Solar power is very promising area of alternative renewable energy source. The further development of photovoltaics requires increasing the efficiency of solar cells (SC) – devices that directly convert light into electric energy [1]. One of the factors determining the low efficiency of SC is the presence of optical losses, mainly by reflection. The conversion efficiency can be increased by optimizing the structure, in particular, the usage of silicon-based heterostructures. Recently the significant capability of a-Si:H/c-Si heterostructure SC was demonstrated, which reached a record efficiency value of 24.7% for the HIT design with contacts on the both side. However, the a-Si:H layer absorbs a significant part of optical radiation and a further increase of the efficiency of heterostructure SC is possible due to the use of wide band gap emitter materials, in particular, GaP. Development and optimization of the structure is required for new GaP/Si structures to reduce optical reflection losses, by applying antireflection (AR) coatings. AR coating is a film that has a lower refractive index than the substrate material. The point of applying an AR coating is to create a dual interface using a thin film that produces two reflected waves, which interfere with each other to achieve low reflection and high transmission. There are many ways to form AR coatings but plasma-enhanced chemical vapor deposition (PECVD) is the most suitable one for combine with SC fabrication process. PECVD deposition could be achieved by introducing NH₃-free SiH₄/N₂ gas mixture into reaction chamber, which are decomposed in a glow discharge plasma. Using N₂ over NH₃ has several advantages, like being abundant, economical, and environmentally safe. In this paper the researches were carried out to determine the possibility of using SiNₓ layers deposited from various SiH₄/N₂ dilution mixtures as an AR coating for GaP/Si photoconversion structures. There is a new type of GaP/Si heterostructures for SCs, for which it is necessary to develop an AR coating, which will also be resistant to annealing at high temperatures [2].

2. Experimental conditions, materials
The depositions of SiNₓ layers with SiH₄/N₂ gas mixture on Si and fused silica substrates were performed by PECVD at 250°C using Oxford instruments Plasmalab 100 setup. Deposition time was fixed to 20 min, N₂ flow equal to 950 sccm, 13.56MHz RF power equal to 88 mW/cm² and SiH₄ flow...
varied from 1 to 6 sccm. To test double layer AR coating capability a 100 nm of SiO₂ layer with refractive index equal to 1.46 was deposited by addition PECVD process from the mixture of SiH₄ and N₂O. The study of the optical properties of SiNₓ layers deposited on silicon and quartz substrates with various deposition conditions were completed by Horiba P2000 laser ellipsometer (at a wavelength of 632 nm) and measurement of reflected and transmitted light (200-1200 nm) with optic fiber CCD spectrometer Avantes 2048. Study of the optical properties of a GaP/Si SC structure with an AR coating on planar and textured silicon substrates were carried out using an Ocean Optics PTFE integrating sphere [3]. To evaluate optical properties of AR coatings AFORS-HET 2.4.1 simulation software was used [4].

3. Results

By the method of optical spectroscopy, transmission spectra of SiNₓ layers with different dilutions of SiH₄/N₂ on quartz substrates were obtained (figure 1). For wavelengths below 700 nm, measurements were carried out using a xenon lamp since it gives large radiation intensity, and for wavelengths above 700 nm using a halogen lamp due to the absence of sharp spectral lines. On all graphs, a clear interference pattern was observed associated with various values of the refractive index of the layer and substrate. For layers grown with a SiH₄ flow of more than 1.5 sccm, a sharp drop in transmission in the short-wavelength part of the spectrum is shown, which is associated with a significant absorption. With a further increase in the SiH₄ flow, the absorption edge shifts toward longer wavelengths. This is due to a change in the stoichiometric composition of the SiNₓ layers and decrease in the band gap of the material. [5]

![Figure 1](image)

**Figure 1.** Transmission spectra of SiNₓ layers on fused silica substrate deposited with different SiH₄ flow.

From the transmission spectra on quartz substrates, the refractive index can be determined using the technique described in detail by Swanepoel [6]. However, due to the presence of absorption and a small number of interference extremes it is not possible to completely restore the spectral dependence of the refractive index. Therefore, calculations were performed only for individual points corresponding to interference minima that located outside the absorption region (figure 3). Refractive indexes for SiNₓ layers with SiH₄ flow equal to 3, 4, 5 and 6 sccm were estimated by Swanepoel method as well as by minimum on Si only for specific wavelength of 2nd order minimum 541 nm, 601 nm, 689 nm and 756 nm respectively.
Figure 2. Reflection spectra of SiN$_x$ layers on Si substrate deposited with different SiH$_4$ flow.

Optical properties of SiN$_x$ layers on Si substrate were studied also by laser ellipsometer at wavelength 632 nm and single incidence angle. The refractive index and layer thickness were determined. For layers grown with a SiH4 flux of more than 1.5 sccm, significant deviations from the values obtained by the previous method were observed. This deviation can be explained by the impossibility of this method of independently determining such parameters as layer thickness, refractive index, and absorption at a specific wavelength. Thus, to determine the thickness and refractive index in the model, a fixed absorption value is set equal to zero, which is suitable only for transparent layers. If there is absorption in the layer, the results of two other parameters may be distorted. To confirm this fact, the third independent method for determining the optical parameters of the layers was used. The reflection spectra for the same layers on Si substrates also show the presence of an interference pattern (figure 2). For a layer with a SiH$_4$ flux of 1.5 sccm on a silicon substrate, the reflection coefficient at a wavelength of 850 nm reaches 0.2%, which makes it possible to use these layers as an antireflection coating. It is well known that the reflection coefficient from a coated surface is expressed in terms of the refractive indexes of the layer, substrate and ambient for a given wavelength according to the formula:

$$R_{\text{min}} = \left(\frac{n^2_{\text{layer}} - n_{\text{sub}} n_{\text{air}}}{n^2_{\text{layer}} + n_{\text{sub}} n_{\text{air}}}\right)^2$$

(1)

From this formula, the refractive index of the layer can be expressed in terms of the known value of the refractive index of the substrate $n_{\text{sub}}$ and the value of the reflection coefficient at the minimum reflection point $R_{\text{min}}$ in decimal units:

$$n_{\text{layer}} = (\pm 2\left(\frac{n_{\text{sub}}^2 R_{\text{min}}}{(1-R_{\text{min}})^2}\right)^{1/2} + \frac{n_{\text{sub}} (R_{\text{min}} + 1)}{1 - R_{\text{min}}})^{1/2};$$

(2)

The uncertainty ± in this formula could be resolved by the well-known dependence of the increase in the refractive index of SiN$_x$ with increasing Si content [7]. Thus, from the minimum of the reflection spectrum of the SiN$_x$ layer on the Si substrate, it is possible to determine the refractive index at a specific point.
Figure 3. The dependence of SiNx thickness and refractive index on the SiH4 flow.

The results demonstrate that an increase of the SiH4 concentration, on the one hand, leads to an increase in the refractive index of SiN layers but, on the other hand, their absorption edge shifts to the visible area leading to an increase in optical losses in this layer. The optimal deposition conditions for design of SC with minimal optical loss have been found (SiH4 flow 1.5 sccm). Using obtained parameters an accurate estimate of double-layer AR coating thicknesses were provided through modeling in AFORS-HET software. The calculated thicknesses obtained for the SiNx and SiO2 layers were 50 and 100 nm, respectively. Numerical modeling showed that at these thicknesses the smallest reflection was observed in the wavelength range of 400-1100 nm, which corresponds to the spectral range of silicon-based solar cells.

Examining of antireflecting properties of the developed SiNx layer were carried out. The SiNx/SiO2 double layer AR coating was deposited on a planar polished and textured surface of GaP/Si structures. The measurements of total reflection from the planar and textured surface were done using an integrating sphere (figure 4).

For this combination of two-layer AR coatings on a planar substrate, it was possible to achieve an average total reflection value not exceeding 7% in the range 400-1100 nm, which is much less than without it (~ 35%). A sharp increase in the reflection coefficient in the long-wavelength part of the spectrum is due to the transparency of Si substrates for infrared radiation and its reflection from the polished back surface. For textured structures, the obtained average value of total reflection was no more than 2.5%. This means that most of the radiation incident on the surface of the substrate will be absorbed in the bulk. Thus, the combination of texturing of silicon substrates and the use of a double-layer SiNx/SiO2 AR coating makes it possible to effectively minimize reflection from the front of the solar cells based on GaP/Si heterostructures.
Figure 4. Full reflectance spectra of a planar and textured GaP/Si SC structure with a SiNₓ/SiO₂ AR coating. The images of the structures surface are presented in the inset.

4. Conclusion
This paper presents the optical properties of SiNₓ layers used as a part of antireflection coating for GaP/Si solar cells. Optical absorption was studied by transmittance measurements performed for the SiNₓ layers deposited on fused silica substrates. For SiH₄ flow >1.5 sccm absorption increases more strongly indicating optical losses. By using methods of ellipsometry and optical spectroscopy, the dependences of the refractive index and thickness on the SiH₄ dilution in N₂ were determined. The obtained dependence of the growth rate is linear, which indicates the growth mode limited by the flow of silane. With an increase in the SiH₄ flow of more than 1.5 sccm, the refractive index increases stepwise from 1.8 to 2.3. Using numerical modeling methods, the structure of an effective AR coating was developed which allows reducing the average value of total reflection from GaP/Si solar cell to 2.5%. In this case, the minimum value of the reflection coefficient reaches 0.7%.

Acknowledgments
The reported study was partially supported by Ministry of Science and Higher Education of the Russian Federation (research project FSRM-2020-0004).

References
[1] Lukutin B V, Surzhikova O A, Shandarova E B 2008 Renewable energy in decentralized power supply (Moscow - Energoatomizdat) p 231
[2] Uvarov A V, Zelentsov K S, Gudovskikh A S 2019 Effect of Thermal Annealing on the Photovoltaic Properties of GaP/Si Heterostructures Fabricated by Plasma-Enhanced Atomic Layer Deposition// Semiconductors 53, 1075
[3] Jacquez J A, Kuppenheim H F 1955 Theory of the integrating sphere (J.Opt.Soc.Am.) vol 45 p 460-470
[4] Varache R, Leendertz C, Gueunier-Farret M E, Haschke J, Muñoz D, and Korte L 2015 Investigation of Selective Junctions Using a Newly Developed Tunnel Current Model for Solar Cell Applications 141, 14–23
[5] Ahmed N, Singh C B, Bhattacharya S, Dhara S, Bhargav P B 2013 Optical and Structural Properties of Ammonia-Free Amorphous Silicon Nitride Thin Films for Photovoltaic Applications 46(7), 493
[6] Swanepoel R 1983 J. Sci. Instrum. 16(12) 1214

[7] Blech M, et al. 2009 Detailed study of PECVD silicon nitride and correlation of various characterization techniques, in Proceedings of the 24th European Photovoltaic Solar Energy Conference and Exhibition (EU PVSEC 2009), Hamburg, Germany p 507-511