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ABSTRACT

Thin films of Si_3N_4 were prepared by non-reactive magnetron sputtering in an Ar atmosphere. A previously synthesized Si_3N_4 was used as a solid-state target. Deposition was carried out on a cold substrate of p-Si (100) with a resistivity of 2 Ohm cm. The Raman spectrum of the deposited Si_3N_4 layers has been investigated. The position of the maximum in the Raman scattering spectrum of Si_3N_4 layers corresponds to the Si_3N_4 compound and the shape of the spectrum is characteristic for the nanocrystalline state of the cubic modification of silicon nitride.

The film thickness has been determined from atomic force microscopy measurements. The results of electron diffraction investigations of $n-Si_3N_4$ nanolayers with thicknesses up to 20 nm demonstrates that as-deposited Si_3N_4 thin films consist of a mixture of microcrystalline and amorphous phases.

Solar cells based on heterostructures consisting of a p-type Si (100) and n-type Si₃N₄ nanolayers were fabricated and studied.

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Introduction

Crystalline Si is still the mostly used material for the fabrication of solar cells (SCs). However, the efficiency of Si SCs has almost reached the theoretical limit. Therefore, the efforts of the scientific community are focused on the elaboration of new types of lowcost photovoltaic (PV) devices. The cost reduction is achieved by simplifying the fabrication technology and reducing the material consumption by using thinner Si wafers. In addition, different nanolayers, e.g., ITO, SiC, Si₃N₄ are used for the preparation of Si based SC heterojunctions [1]. Such devices are usually based on metal-insulator-silicon (MIS) surface barrier structures with an inversion layer (IL) located in silicon near the heterojunction interface [2]. As Si₃N₄ is one of the key materials in microelectronics, Si₃N₄ thin films become also of particular interest for SC manufacturing. Si₃N₄ was introduced for the first time into PV for the fabrication of MIS/IL solar cells as early as the 1980s. Further investigations showed that very low surface recombination velocities can be achieved using Si₃N₄ films in SC fabrication, while using these films also as antireflection (AR) coatings. Si₃N₄ films are mainly prepared by chemical vapor deposition (CVD), plasma-enhanced chemical vapor deposition (PECVD), electron cyclotron resonance, or reactive magnetron sputtering (RMS). Even though CVD is widely used for obtaining those films, the main disadvantages of this technique are the incorporation of H₂ in the films and high substrate temperatures. The entrapped hydrogen in the films can deteriorate the properties of Si₃N₄ and therefore a high substrate temperature is generally undesired in microelectronic applications. Si₃N₄ films with extremely low hydrogen content can be prepared by RMS at a low substrate temperature. Especially promising for the deposition of Si₃N₄ thin films is the high-frequency non-reactive magnetron sputtering (HFNRMS) because it is a non-toxic and a low material consumption deposition method. Moreover, widespread and reasonably inexpensive equipment allows obtaining high quality Si₃N₄ nanofilms [3]. Hence, the aim of this contribution is the demonstration of the possibility to fabricate MIS/IL SCs by a simple and low-cost HFNRMS technology using Si₃N₄ nanolayers.

Materials and experimental method

Thin films of Si_3N_4 were obtained by the HFNRMS method using the Ukrrospribor VN-2000 setup. A previously synthesized silicon nitride was used as a solid-state target. The deposition was carried out on a cold substrate of p-Si (100) with a resistivity of 2 Ohm cm. The layer of silicon oxide was removed from the Si substrate by chemical etching in HF before the Si_3N_4 film deposition. Si_3N_4





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nanolayers with the thickness up to 20 nm were obtained. The composition of deposited layers was characterized by Raman Spectroscopy (RS) techniques using co-focal nanometric resolution Omega Scope AIST-NT Raman microscope excited with a 532 nm Ar⁺ laser. The position of the maximum in the spectrum of Raman scattering corresponds to the cubic modification of silicon nitride [4]. The electron diffraction investigations were carried out on thin foils of Si₃N₄ nanofilms in a high resolution (2 Å) transmission electron microscope (TEM) JEOL JEM-2100. This study demonstrates that Si₃N₄ films, deposited on the Si surface by HFNRMS, are a mixture of microcrystalline and amorphous states. Diffusion rings around the central reflex are the evidence that the film material is predominantly of amorphous character, while not-well defined concentric rings denote the presence of the second phase of a nano- or microcrystalline state. Measurements of the thickness and surface morphology of Si₃N₄ films were performed using a scanning probe microscope (SPM) and an atomic force microscope (AFM) (NTEGRA Aura, NT-MDT) in a controlled atmosphere of a partial vacuum.

$p\text{-}Si/Si_3N_4\text{-}nanolayer photovoltaic cells: preparation and characterization$

We have prepared a heterojunction photovoltaic cell consisting of a substrate of p-type Si (100) covered by a layer of n-type Si₃N₄. The Si substrate was specially treated with chemical etchants before the Si₃N₄ layer deposition. The best results have been achieved with Si₃N₄ layers with the thickness of 20 nm. Onto silicon nitride thin film an Ag/Cu grid has been deposited as top electrode. A continuous Ag:Cu layer has been deposited as back electrode. The cross-section schematic of the solar cell device is shown in Fig. 1.

The dark *I*–*V* characteristic of the elaborated p-Si/n-Si₃N₄ SCs is presented in Fig. 2 The devices were studied by performing dark *I*–*V* measurements and investigating spectral dependences of the SCs photo sensitivity as well as by measuring illuminated *I*–*V* load characteristics under AM1.5 standard conditions (1000 W/m²,







Fig. 2. Dark I-V characteristic of a p-Si/n-Si₃N₄ SC.



Fig. 3. Load *I–V* characteristic of a p-Si/n-Si₃N₄ SC.

25 °C) with an ST-1000 solar simulator. The barrier height at the Si/Si₃N₄ interface estimated from dark *I*–*V* measurements in the temperature range of 300–450 K varied between 0.9 eV and 1.0 eV. These values are much higher than the half of the Si band gap. Therefore, we conclude that a MIS/IL type SC is obtained and that the entire space charge region, where the light absorption takes place and charge carriers are generated and separated, is located in Si. This fact is in addition confirmed by the spectral dependence of the Si/Si₃N₄ photosensitivity, which entirely corresponds to the respective characteristic of Si SCs. In Fig. 3 an *I*–*V* load characteristic of a Si/Si₃N₄ SC is presented. From this *I*–*V* curve the solar cell PV parameters were determined: the short-circuit current density of 18.6 mA/cm², the open circuit voltage of 0.538 V, the fill factor of 51% and the efficiency of 6.38%.

Conclusion

A heterostructure was obtained by HFNRMS of a Si_3N_4 nanolayer on the surface of p-type Si wafer. Based on this heterostructure, SCs were fabricated.

The investigation of the electric and photoelectric properties of the p-Si/n-Si₃N₄ nanolayer SCs shows that a MIS/IL SC is formed. The barrier height at the Si/Si₃N₄ interface is 0.9-1.0 eV.

The spectral dependence of the Si/Si₃N₄ SC photo sensitivity entirely corresponds to the respective characteristic of the Si solar cell. Load I-V characteristics of the elaborated SCs demonstrate conversion efficiencies of 6.38%.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.rinp.2016.01.003.

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