Electrochemically deposited ZnO nanostructure on ZnO:V seeding layer

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Abstract. ZnO nanostructured (NS) arrays are grown by electrochemical method on conductive seeding layers of ZnO doped with V (ZnO:V) deposited by magnetron sputtering on glass substrates. The surface morphology of the ZnO NS is studied by Scanning Electron Microscopy. The spectra of transmittance, diffused and specular reflectance are measured for the ZnO NS arrays deposited for 30 and 60 min. and are compared to the corresponding spectra of the substrate with seeding ZnO:V film. The values of diffused reflection are higher than those of the seeding layers due to the growth of nanostructured ZnO arrays. Increasing of the diffused reflection with the time of electrochemical growth is observed and is explained by increasing size of the grains. The results show the possibility for deposition of nanostructured ZnO arrays on low cost ZnO:V seeding layers with large effective surface area that could be applied in thin film solar cells for increasing light harvesting.

1. Introduction

Nanostructured semiconductor materials have attracted the interest of the researchers due to their potential for different innovative applications, e.g. in solar cells [1] as an n-type electrode [2], near UV-leasers [3], field effect transistors [4], gas sensors [5], etc.

Application of the nanomaterials in the architecture of thin film solar cells started with proposed by M. Green idea [6] for development of the third generation solar cells. The goal is the development of thin films low cost technology for solar cells and modules with higher efficiency. One way is the development of the preparation methods and study of properties of nanomaterials for applications in solar cells for improvement of the light harvesting and their efficiency.

ZnO is one of the most attractive semiconductor materials which can be produced in thin film with different nanostructured modifications [7, 8].

Different substrates have been used for growing ZnO nanostructured arrays such as ITO on glass, c-Si [8], multicrystalline Si [7], Cu plates [7].

In this work the results of study of the structural and optical properties of ZnO nanostructured arrays grown by electrochemical method on seeding conductive ZnO:V thin films are presented.

2. Experimental
Thin ZnO:V films were prepared by R.F. magnetron co-sputtering of ZnO target (10 cm diameter) with pieces of vanadium chips on in the maximum erosion zone of its surface in Ar atmosphere at a pressure of 0.5 Pa and r.f. power of 150W as described in [9,10]. The films were deposited on corning glass without heating of the substrates. The thickness of the ZnO:V films used as seeding layers for electrochemical growth of ZnO NS’s was 600 nm. The concentration of V was 1.41 % and the sheet resistance - 26 Ω/cm².

ZnO nanostructured films were deposited on the ZnO:V seeding layer by electrochemical process from aqueous solution of ZnCl₂ (5x10⁻⁴ M) and KCl (1 M) with pH≈5.0 at 70°C for different deposition times: 30 and 60 min using a three-electrode electrochemical cell with SCE as a reference electrode. Spectrally pure graphite rod electrode was applied as anode. The electrolyte was agitated by magnetic stirrer. The process was carried out controlling the redox potential of the high power potentiostat system WENKING HP 96. The deposition potential was kept at -1000 mV (vs. SCE). Good quality ZnO films were obtained at a redox potential within the range between +0.300 and +0.400 V (vs. SCE). At a redox potentials higher than +0.4 V (vs. SCE) Zinc peroxide (ZnO₂) was formed on the samples with bad adhesion to the substrate. The oxygen content in solution was permanently measured, oxygen is provided in the system by supplement of H₂O₂.

The study of the surface morphology of the deposited ZnO nanostructured arrays was performed by a Scanning Electron Microscope (SEM) Philips 515. The optical spectra (transmittance, specular reflectance, diffuse reflection) of the deposited arrays were measured by a spectrophotometer Shimadzu UV-3600 in the range of 320 - 1800 nm employing a 60 mm integrated sphere.

3. Results and discussion
Figure 1 shows SEM surface and cross section images of the ZnO:V seeding layer. The SEM pictures show a dense column structure of the films with diameter of the column about size 30 nm.

![SEM of the seeding ZnO:V layer: plane (a) and cross section view (b).](image)

3. Results and discussion

Figure 1. SEM of the seeding ZnO:V layer: plane (a) and cross section view (b).

The surface morphology of the ZnO structures grown electrochemically for 30 and 60 min on these seeding layers is presented on figure 2.

It can be seen from figure 2 that ZnO structures deposited for 30 min consist of: grains with diameters of about 1 – 2 µm grown between thin walls that look like whiskers. These walls have different lengths—from 1 to 10 µm and thickness of about 200 nm. An increase in the deposition time to 60 min leads to increasing the number of the grains with size about 1 µm, some of them coalesce between them and with the walls as a result larger grain areas of about 3-4 µm are formed. The height of the grain increases from about 0.5 µm to 1 µm with deposition time increasing till 60 min.
Figure 2. SEM pictures of the ZnO nanostructures grown on ZnO:V seeding layer for different deposition time (a, b and c) - 30 min, and (d, e and f) – 60 min; pictures (a, b, d and e) shown - surface view, and pictures (c) and (f) shown cross section. The markers in the pictures (a and d) correspond to 10 µm and in the pictures (b, c, e and f) correspond to 1 µm.

The spectra of transmittance, specular reflectance and diffused reflection of the ZnO nanostructured area layer are presented in figure 3 a, b, c, respectively. The spectra have been recorded in the optical range of 320 – 1800 nm. For comparison, the corresponding spectra of ZnO:V seeding layer are presented as well. The values of transmittance and specular reflectance of the samples with deposited ZnO nanostructure decrease in the visible and near IR range compare to the value of the substrate. However the values of diffused reflection are higher compare to value of the seeding layer and increase with the time of ZnO electrochemical deposition due to the more developed surface of the deposited ZnO nanostructured arrays – the grains become bigger.

Figure 3. The spectra of transmittance (a), reflectance (b) and diffused reflection (c), of the ZnO nanostructured electrochemically deposited layer for different time: 30 min - curves 2 and 60 min – curves 3. For comparison the spectra of ZnO:V seeding layer are shown – curves 1.

Similar results have been reported for deposition of ZnO NS array on other substrate materials, such as multicrystalline Si [7, 11]. The layers grown on low cost ZnO:V substrate can be considered as supporting substrates for deposition of a-Si:H, poly-c-Si, organic etc. thin film based solar cells.
4. Conclusion
It is demonstrated for first time, that conductive ZnO:V thin films can be used as seeding layers for nanostructured ZnO arrays grown by electrochemical deposition. It is observed that ZnO nanostructures consist of grains and wiskers. An increase of the diffused reflection compared to that of the seeding ZnO:V layers is due to the nanostructures grown. With increasing of the time of deposition the nanograins increase in size leading to formation of more developed surface and increased values of the diffused reflection.

Although further optimization of such ZnO NRs based structures is required, the obtained results can be considered as a promising technological development towards low-temperature and cost effective technology for the processing of substrates in thin film based solar cells with improved light harvesting.

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