Investigation of the Visible Light-Sensitive ZnO Photocatalytic Thin Films

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***Abstract*—ZnO photocatalytic thin films deposited on a glass substrate are obtained by chemical spraying technique, and they are active in the visible light spectrum. Optical studies have shown that ZnO thin films doped by nickel impurities absorb visible light at wavelengths from 400nm to 600nm. At the same time, this absorption rate increases with the increase of concentration of nickel impurities. At high concentration (5%), the absorption of light is reduced in the visible area, but after heat treatment at 600^{0}C the light absorption in these samples improves, which allows us to conclude that the observed effect is caused by a violation of the homogeneity of the distribution of nickel impurities and the creation of agglomerates. Decoration of ZnO thin film surfaces by silver clusters improves light absorption, as it happens to the nanopowders, but in the case of thin films, this effect is much smaller. Experiments on methylene blue determine the significance of photocatalytic activity in the visible area of sun irradiation of ZnO thin films containing nickel impurities, which are obtained by chemical spraying technique.**

Keywords—thin films; ZnO; impurities; photocatalysis; ecology

I. INTRODUCTION

Photocatalysis is the activation of reduction-oxidation (redox) reactions due to the influence of light. The reaction is connected to specific substances, called photocatalysts. Photocatalysis can be used for the decomposition of water in hydrogen and oxygen and for the degradation of harmful substances in water and air under sun exposure [1]. As a result of light irradiation, a semiconductor photocatalyst particle generates electron-hole pairs that can reach the surface of the particle, enter in the redox reactions with environmental molecules and cause their dissolution, e.g. water dissolves into oxygen and hydrogen. Hydrogen, obtained from water, can be used as an environmentally friendly fuel with the final product of its combustion being water again. Photocatalysis can also decompose organic molecules, including bacteria, into the environment, and result in carbon dioxide, oxygen, and water. This is the main reason of the ongoing research for photocatalysis usage in hydrogen energy, ecology, and medicine [2-7].

The low efficiency of the reaction is the main challenge, which prevents the wide practical usage of photocatalysis. This is caused by two reasons: 1. Low quantum yield brought by recombination of electrons and holes and 2. Low level of visible light usage in photocatalysis, which has ten times more energy in the solar irradiation than its UV share, caused by the large width of energetic gap in a stable photocatalist. To improve the quantum yield, small clusters of different materials, so-called co-catalists, are coated on the surface of photocatalist particles, which capture electrons and holes, and thus, reduce the recombination [8]. Introduction of various impurities in photocatalists, which decreases the width of energy gap is the main method of increasing the amount of visible light in the process of photocatalysis [9, 10]. A photocatalytic reaction occurs on the surface of the photocatalyst. Therefore, photocatalysts are generally used in the form of powders to increase surface area. However, photocatalytic thin films are frequently needed as well, especially when the photocatalysts are used for environmental purposes, since these substances are often necessary in continuous flow systems, and it is very difficult to separate photocatalytic nanoparticles from a suspension. The thin photocatalytic films are also necessary to obtain self-cleaning surfaces, e.g. to create lamps that do not get attached with soot in automobile tunnels, smart window glasses, etc.

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Currently, research is underway to create new photocatalytic thin films of various substances that are active in the visible region of solar radiation and therefore have improved efficiency. Authors in [11] prepared pure CdS and Cu-doped CdS thin films using the spray pyrolysis technique while 2%, 4% and 6% Cu-contents were used for doping. Reflectance and transmission measurements were studied in the spectral range of 200–1100nm to extract the optical properties variation upon copper doping. Authors in [12] developed successful strategies on combining the versatility of mechanochemical synthesis with rf-sputtering for the controllable deposition of $BiVO_4$ thin films. Photocatalytic activity experiments were performed for the degradation of rhodamine 6G (Rh6G) dyes under visible light irradiation. Authors in [13] investigated the long term stability and photocatalytic activity of Cu_2ZnSnS_4/TiO_2 thin film heterostructures, under simulated solar radiation, using phenol and imidacloprid as testing pollutants.

Our group conducted studies on the sensitization of thin photocatalytic films to visible light similar to those described above. ZnO photocatalytic thin films doped by nickel impurities and obtained by chemical spraying were studied. This choice was due to the fact that despite its relatively low photocatalytic efficiency, ZnO possesses a number of unique properties which make it one of the strongest candidates for industrial use, if it is sensitized to visible light and therefore has increased efficiency. These properties are: non-toxicity, direct forbidden gap at room temperature (3.37eV), decent optical properties, chemical resistance to photoreactions, low cost, etc.

II. EXPERIMENTAL PART

ZnO thin films were deposited onto glass substrate at 460°C by spray pyrolysis [14]. Undoped ZnO thin films were prepared using a zinc acetate precursor ($C_4H_6O_4Zn.\ 2H_2O$) dissolved in 2-propanol to obtain a starting solution with a concentration of 0.1mol/l. Nickel-doped ZnO thin films were prepared by adding a compound source of nickel chlorure hexahydrate ($NiCl_2(6H_2O)$, 99.9% purity) to the precursor solution while maintaining the acidity level for atomic percentages of [Ni]/[Zn] of 1,2,3,4,5 wt%. These samples are presented in Figure 1.

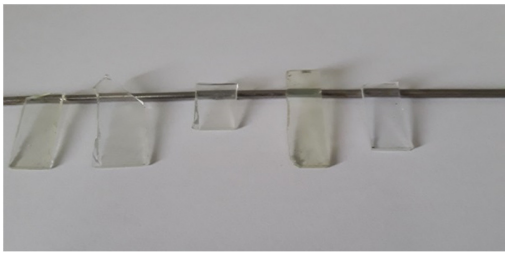

Fig. 1. ZnO:Ni thin film samples deposited on glass

ZnO:Ni thin films coated by silver clusters were obtained by a novel technology developed in the Andronikashvili Institute of Physics at Ivane Javakhishvili Tbilisi State University, which consists of depositing metallic clusters on the surfaces of the nanoparticles of fine powders [15, 16]. The technology was modified for Ag nanoclaster deposition on the surface of ZnO:Ni thin films. This inexpensive electroless technology proceeds at low temperatures (50-60^{0}C) and hence it does not change either the coated material or the material of clusters itself. A solution of the following composition: $AgNO_3$ – 0.7g/l, NH_4OH – 7ml/l, NaOH – 0.8g/l was prepared for this purpose. KNa was added right before the experiment started. KNa amount and deposition time determine the size of coated nanoclasters. Scanning Electron Microscope (SEM) and Energy Dispersive Spectroscopy (EDS) investigations were conducted on the SEM TESCAN VEGA3 XMU, which is equipped with Energy Dispersive Spectrometer (EDS): Oxford Instruments, AZtecOne (Figure 2).

Fig. 2. SEM VEGA3 equipped with EDS of Oxford Instruments

III. RESULTS AND DISCUSSIONS

Light absorption increases in the visible area during the introduction of nickel impurity in ZnO thin films. When this process was observed, the detailed studies started by ZnO thin films been deposited on a glass substrate of uniform thickness, containing different amounts of Ni impurities prepared beforehand, and their structure and optical spectra were studied afterwards. The concentration of Ni impurities varied from 1% to 5% with a 1% step. The SEM and EDS investigation results of these samples are shown in Figures 3 and 4 respectively. The SEM image of the ZnO:Ni thin film (Figure 3) shows that the surfaces of the films are quite smooth. The EDS image of the ZnO:Ni thin film with 3% Ni content (Figure 4) points out the existence of other impurities apart from Ni in the ZnO sample.

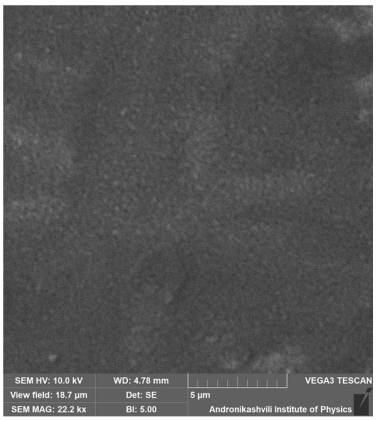

Fig. 3. SEM image of the ZnO:Ni thin film with 3% Ni content and deposited on the glass

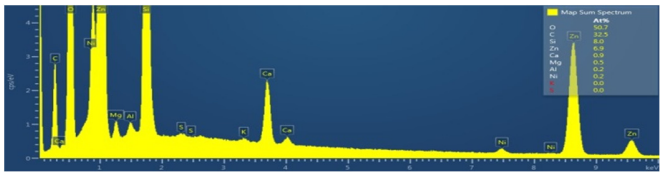

Fig. 4. EDS spectrum of the ZnO:Ni thin film with 3% Ni content and deposited on the glass

The ZnO:Ni film sample may contain a part of these impurities while the rest of it may be in a glass substrate. To clarify this situation, the similar EDS spectrum of the glass without ZnO:Ni thin film was obtained, which showed that there were only Ca and K additional impurities in the ZnO film itself. Figure 5 shows the experimental results of the optical investigations. It has to be noted that there are no results below 400nm, because ZnO thin films have been deposited on the glass and hence the optical properties of the films in this area could not be studied because of the strong absorption of ultraviolet rays by the glass. The experiments have shown that the absorption of light by ZnO with the introduction of Ni impurities increases with the increase of the concentration of Ni impurities from 1% to 4%, in the visible area at the wavelength range of 400nm to 600nm. When the concentration of impurities increases further, e.g. at the nickel concentration of 5%, the light absorption decreases at this wavelength interval. Figure 5 also shows that Ni plays the main role in increasing the absorption of light in the visible area while the other impurities which exist in the ZnO film have considerably less influence in the existing amounts.

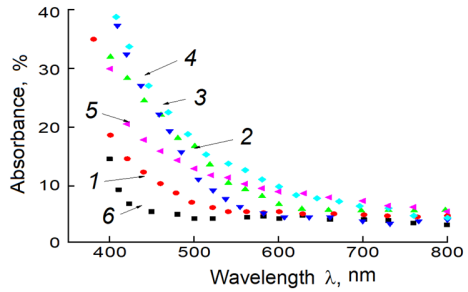

Fig. 5. Dependence of the optical spectrum of ZnO thin films on the concentration of nickel impurities. Curve-1: ZnO with 1% content of Ni impurities, curve-2: ZnO with 2% Ni, curve-3: ZnO with 3% Ni, curve-4: ZnO containing 4% Ni, curve-5: ZnO containing 5% Ni, and curve-6: ZnO without nickel impurities

The image on Figure 5 is quite complicated, so to make this process more visible, the dependence of light absorption rate on the concentration of impurities at a specific wavelength of 450nm has been built for nickel-containing zinc oxides. Figure 6 (continuous line) shows this dependence graph, which clearly indicates that as the nickel concentration increases up to 4% the absorption rate increases too, but at 5% it decreases sharply (continuous line and dot a). It was suggested that the reduction (shown on Figure 6) in light absorption at high concentrations of impurities should have been caused by the inhomogeneous distribution of these impurities and by the creation of their agglomerates. In order to test this assumption, heat treatment was carried out on a sample containing 5% Ni in vacuum at 600^0C for 1 hour. The goal of the test was to remove the aforementioned agglomerates. Figure 6 (dash line and dot b) shows the absorption value of this sample at a wavelength of 450nm after thermal treatment in a vacuum. As it is clear from Figure 6, the absorbance has been increased sharply at 450nm after the vacuum thermal treatment at 600^0C, confirming our assumption.

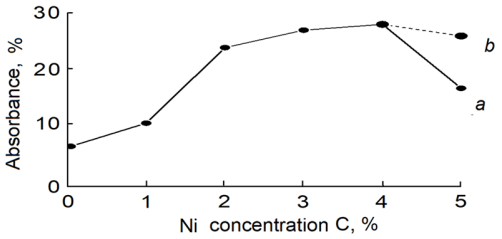

Fig. 6. Dependence of light absorption of zinc oxides with nickel-impurities on nickel concentration at 450nm wavelength before heat treatment (continuous line and dot- a) and after heat treatment (dash line and dot- b)

As mentioned above, one of the main methods of increasing the quantum yield of photocatalyst nanopowders is to place different nano-size clusters on the surface of their particles which would capture photo-induced electrons and holes and reduce their recombination. To hit the goal in our case, silver clusters were placed on the surface of ZnO thin films with Ni impurities and their optical properties have been investigated. Figure 7 shows the results of the corresponding investigations: curve 1 corresponds to the absorption spectrum of ZnO thin film containing 3% of nickel impurities before decorating its surface with silver clusters and curve 2 does the same after decorating its surface.

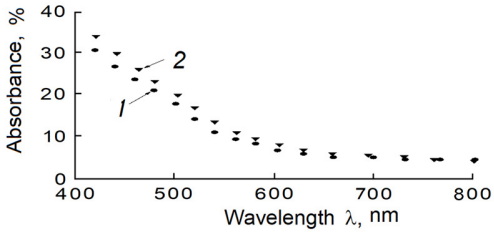

Fig. 7. Change of the absorption spectrum of ZnO thin film by decorating its surface with silver clusters. Curve 1: The black circles show the absorption spectrum before ZnO thin film decoration. Cutve 2: The black triangles show the absorption spectrum after the ZnO thin film was decorated with silver clusters

There is an obvious increase in the light absorption after the clusters are applied to the surface, but the effect is much smaller than in the case of decorating nanopowders [17]. We suggest that the reason is that the surface area is much larger in the case of nanopowders than in the case of thin films. Figure 8 shows the results of the investigation of the photocatalytic activity of the ZnO thin film with nickel impurities in the visible area of sunlight. Methylene blue solution has been used to evaluate the photocatalytic activity. By changing the methylene absorption in this solution at 665nm wavelength, methylene degradation has been observed. Two glass vessels of 5ml methylene blue were used for the experiment. It was spectrophotometrically established that the glass vessels hardly

allowed the ultraviolet rays with less than 38nm wavelength to pass through. One vessel contained only a solution of methylene blue while another vessel contained the same solution of methylene blue with a thin layer of ZnO containing 4% nickel impurities deposited on glass substrates. The surface area of ZnO:Ni thin film with 4% Ni content was approximately 1cm^2. Both vessels were placed under the summer sunlight at 30^{0}C for six hours. After each hour of solar irradiation the methylene blue solution from the glass vessels was placed in the spectrophotometer cuvette and the concentration of methylene blue was determined in the solution using methylene absorption peak value at 665nm wavelength. The spectrophotometer was pre-calibrated and the methylene concentration dependence on the absorption peak value was plotted. Using this graph the concentration of methylene was determined according to the amount of absorption. The experiments showed that the concentration of methylene remained almost unchanged in the vessel without the ZnO thin layer, whereas the concentration of methylene gradually decreased in the vessel containing the ZnO thin layer. Figure 8 illustrates the results.

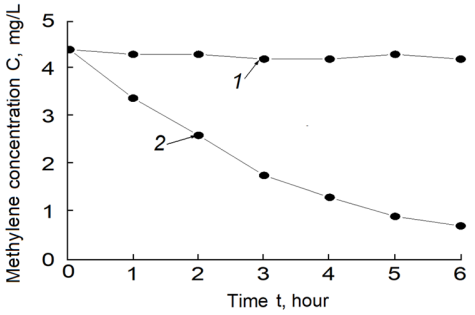

Fig. 8. The graph of methylene blue degradation by the action of visible light. Curve 1: Without the thin film of ZnO in the vessel. Curve 2: The vessel contained a thin film of ZnO with 4% nickel impurities

IV. CONCLUSION

Photocatalytic ZnO thin films active in the visible light were obtained by spray pyrolysis technique when hydrated Ni chloride hexahydrate $NiCl_2(6H_2O)$ was added to the precursor solution. Optical investigations have shown that Ni impurities enhance the absorption of light by ZnO thin films in the visible area from 400nm to 600nm wavelength and this absorption increases with the increase of the concentration of Ni impurities. Also, it has been established that the formation of agglomerates of the impurities at high concentrations reduces the light absorption. The light absorption gets increased when the surfaces of ZnO thin films with Ni impurities are decorated with silver clusters but the effect is much smaller than in the case of nanopowders. Experiments on the determination of photocatalytic activity using methylene blue have shown that ZnO thin films with nickel impurities are characterized by photocatalytic activity in the visible area of sunlight.

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