Among transparent conducting oxide materials, the antimony doped tin-dioxide (ATO) films find wide applications due to their excellent properties. They have high mechanical, chemical and environmental stability and are characterized by high electrical conductivity, 90% transparence in the visible region and remarkable reflectivity in infrared region. These films are raw materials for sensors, solar cells, liquid crystal displays, luminescent lamps, protecting layers for the glass substrates, and saturated calomel electrode as a reference electrode.

The films prepared in such way are amorphouse and are transformed into a nanocrystalline coating by a heat post-treatment.

In the CVD process the substrate was heated to 425°C and maintained in the reactor at this temperature for 10 min. The carrier gas was nitrogen with a flow rate of 1 l/min. In this method after cooling the resulting ATO films to room temperature, they were submitted to a thermal post-treatment at 360°C for 45 min.

Characterization techniques
Composition and crystal structure study: X-ray diffraction (XRD) measurements (Philips PW 3710, Kα Cu) for CVD coatings and X-ray photoelectron spectroscopy (XPS) (EA 125 Omicron) for sol-gel coatings.

AFM Investigation
The surface morphology of samples was investigated by contact mode atomic force microscopy (AFM). The tests were carried out using a Nanoscope Dimension 3100 AFM with a Nanoscope III a controller under software version 4.43r8.

Nanoindentation
The mechanical properties of the SnO2 layer were measured by a Hysitron Triboscope nanoindenter. The indenter-transducer of the equipment was mounted in place of the AFM scanner in the Nanoscope Dimension 3100. Depth sensing hardness tests were performed between 4 and 12 mN load.

Electrical conductivity measurement
The sheet resistance measurement of ATO coatings was performed using the four-point method and a self-made device. The carrier charge numbers were determined by the Mott-Schottky equation, measuring impedance at 1000 Hz. The electrochemical impedance was measured using Solartron 1286 electrochemical impedance (ECI) and Solartron 1250 (FRA). Experiments were done in a three-electrode cell using a platinum net as a counter electrode and saturated calomel electrode as a reference electrode. The working electrode was the ATO film on glass.
Transmittance investigation

The transmittance spectra were recorded in the 200-900 nm wavelength range using a Pye-Unicam UV-VIS spectrophotometer.

Potentiodynamic measurements of corrosion potential were performed using a computer controlled potentiostat Model PG STAT 10 from Autolab (Netherlands) in a conventional three electrode electrochemical cell equipped with an Ag/AgCl, KCl sat (Radiometer, France) as reference electrode and a platinum sheet as counter electrode. The working electrode was 1 cm² glass covered by ATO films. The concentration of the solutions for the chemical corrosion tests was 1 M.

Results and discussions

The morphology and crystalline structure of ATO coatings deposited on glass are very important because the film stability is affected by the quality of the surface (uniformity, roughness, adhesion to the substrate) and in the same time by the characteristics of the structure (crystallinity, amorphity and the grain size).

In addition, AFM investigations point out the uniformity of the ATO coatings on the glass. However, the thickness of ATO films prepared by sol-gel method is smaller compared to those obtained by chemical vapor deposition.

In the figure 1 were presented three dimensional (3D) AFM images (1a-SG; 1b-CVD).

The images show dense, continuous and homogenous ATO deposits with a few superficial cracks on the surface. The sample prepared by CVD method contains smaller particles also in homogeneous distribution.

For hardness test of thin films and coatings the so called nanoindentation method was developed which enables the hardness measurement and the determination of the elastic modulus on these samples.

The relaxed nanoindentation impressions were imaged by AFM as shown in figure 2. The impressions show different character: the impression in the substrate has sharp edges and small pile up around the indenter (fig 2a), while the coated samples have smooth edges and obviously a shallower depth than the one in the substrate (fig. 2b, 2c).

The CVD and SG samples have remarkable good properties: satisfying hardness (CVD-5,9 Mpa; SG-5,5 Mpa), low electrical resistance (CVD-30, SG-28 ohm), the charge carrier numbers approach the value established for metals (CVD-4.6 x 10⁻²⁰, SG-4.0 x 10⁻²⁰ n/m²) and very high transmission in visible region (CVD-83, SG-81 %).

In all cases the adhesion of the films to the substrates caused by the Si-O-Sn type bonds is satisfactory.

The chemical composition of the ATO film is demonstrated by XRD and XPS determination. The XRD investigations confirmed that Tin and Antimony were found in the oxidation form SnO₂ and Sb₂O₄. In the same time XPS measurements reveal that at the surface of the film contains Sn and Sb.

The results of XPS show that the sample surface is contaminated by carbon and chlorine. The presence of carbon ions can be explained by the fact that they appear from the contamination of the film from the laboratory environment (organic substances, vapors). Regarding the chlorine contamination, we can say that this element could be provided from the precursor solution.

The chemical stability

The chemical stability in different chemical media (1 M HCl, NaCl, HOCI) was investigated, during a 90 days period, by the following processes: the evolution of the sheet resistance (ρ) (the Vis optical transmittance (T) and the corrosion potential (E).

The effect of the exposure of the ATO films to these degrading media is important because the films are used in chemical industry as protective layers against aggressive media. The experimental results of these studies are shown in tables 1 and 2.

From these results we can conclude: the monthly corrosion rate is very low for all samples, the stability in all three media is very good. The ATO films obtained by CVD and SG have no degradation during the first 30 days of treatment.

It is well known the mechanical and chemical stability of ATO films, which provide a long lifetime for them.
The single degrading media for these films is the nascent hydrogen. This is specially important at the SnO$_2$ joint film for multilayer solar cells, because the presence of metallic Sn and the SnO (appeared at the reduction of the SnO$_2$ at the joint) seriously reduce the light absorbance in the solar cell active surface.

The results of the variation of ATO films characteristics function of curing time with nascent hydrogen are given in table 3.

The 30 s nascent hydrogen treatment do not affected the layer. After this period the thickness of the layer decreases very much quickly, the film resistance substantially increases and the optical transmittance diminishes to the half of starting value.

**Conclusions**

Among transparent conducting oxide materials, the antimony doped tin-dioxide (ATO) films find wide applications due to their excellent properties.

The AFM images show a dense, continuous and homogenous ATO deposits with a few superficial cracks on the surface with spherical nanoparticles.

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**Table 1**

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**Table 2**

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**Table 3**

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<td>Electrical resistance (ohm)</td>
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<td>Transmittance (%)</td>
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The both CVD and SG samples have remarkable good properties: satisfying hardness, low electrical resistance, the charge carrier numbers approach the value established for metals and very high transmittance in Vis region. In all cases the adhesion of the films to the substrates, caused by the Si-O-Sn type bonds is satisfactory.

The AFM and XRD analysis proved for all ATO coatings the crystalline, tetragonal cassiterite structure. Based on these investigation it was confirmed that Tin and Antimony were found in the oxidation form SnO₂ and Sb₂O₄.

We can conclude: the monthly corrosion rate is very low for all samples, the stability in all three media is very good. The ATO films obtained by CVD and SG have no degradation during the first 30 days.

The 30 s nascent hydrogen treatment does not affected the layer. After this period the thickness of the layer decreases very much, the film resistance substantially increases and the optical transmittance diminish to the half of it’s starting value.

Based on these results, we can recommend the use of CVD and SG films as protective coatings.

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