ELECTROCHROMISM IN Au-NiO FILMS

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Electrochromic materials exhibit significant, reversible optical absorption at visible wavelengths when controlled electrochemically [1].

Among the electrochromic materials, nickel oxide is one of the best for applications in display devices, smart windows, batteries and gas sensors due to its high stability under cycling [2]. Nickel oxide is an anodic coloring material that changes color from light gray to dark brown.

It is known that the incorporation of metallic particles in transition metal oxide films alters the optical absorption in the visible region [3].

Theoretical studies were carried out and proved that Au-NiO films have selective absorption in the visible region [4]. Different from the original NiO transmitted/reflected color was obtained by the addition of gold nanoparticles inside the oxide matrix [5].

Different methods of deposition are used to deposit composite films. Among them, sputtering, sol-gel, dip coating and spin coating are the most utilized.

The aim of this work is to characterize electrochemically composite gold-nickel oxide films obtained by three different methods: (*i*) sputtering, (*ii*) sputtering + *sol-gel* and (*iii*) sol-gel and dip coating. The Au-NiO films were deposited by reactive *dc* magnetron sputtering from Au and Ni targets in an Ar + O_2 atmosphere in multi-layered deposition steps. By combination of sputter-deposited nickel oxide films and gold nanoparticles, deposited by the sol-gel and dip-coating methods. And also, the gold-nickel oxide films were prepared by sol-gel and dip-coating in a multi-layered process.

The sputtering deposition was carried out by varying the total pressure inside the deposition chamber, *i.e.*, p = 2.0 mTorr < *p* < 10.0 mTorr. The sol-gel films were prepared by dip-coating on In_2O_3:Sn conducting glass plates at 12 cm·min^{-1} and at 40°C. The films were annealed in air at 250°C for 5 minutes.

The simultaneous measurements of the I *vs.*V plot and spectral transmission of the films, cycled in a 0.1M KOH solution, were recorded with an optical fiber spectrometer (Dual Fiber Optic Spectrometer, S2000 Series) equipped with a DT-1000 Deuterium Tungsten Source from Ocean Optics. The scanning rate was 10 mV·s^{-1} and the spectra were taken every 20 seconds, after ten stabilization anodic/cathodic cycles.

The cyclic voltammetry measurements showed that all the samples did not have a significant electrochemical activity under the initial intercalation/de-intercalation cycles. With increasing number of cycles, there was a constant increase in the number of species intercalated/de-intercalated in the films.

The charge capacity of the NiO_x film deposited by the sol-gel method is much larger than that presented by the NiO_x film deposited by sputtering. This difference can be associated to the larger porosity and crystalline structure of the material deposited by the sol-gel method. The sputtered films are polycrystalline, while the ones deposited by sol-gel and dip-coating are amorphous.

Fig. 1 shows the *in situ* spectral transmittance of the NiO_x films deposited by sputtering and sol-gel plus dip-coating methods. The difference between the bleached and colored states is much larger for the NiO_x film grown by *sol-gel*. The addition of gold in the oxide matrices gives rise to different reflected/transmitted colors (blue and red). These colors depend on the Au particle sizes and the matrix in which the particles were added, as can be seen in Fig 2, especially in the case of Au and NiO_x deposited by the sol-gel method. The particle sizes were estimated by SAXS measurements and confirmed by TEM experiments [6].

Therefore, the color of Au-NiO_x films can be tailored by the use of pre-determined growth conditions.

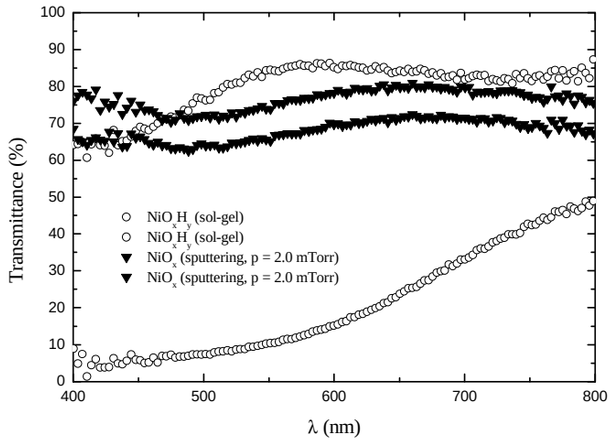

Fig. 1 – *In situ* spectral transmittance of the NiO films grown by (*i*) sputtering and (ii) sol-gel + dip-coating.

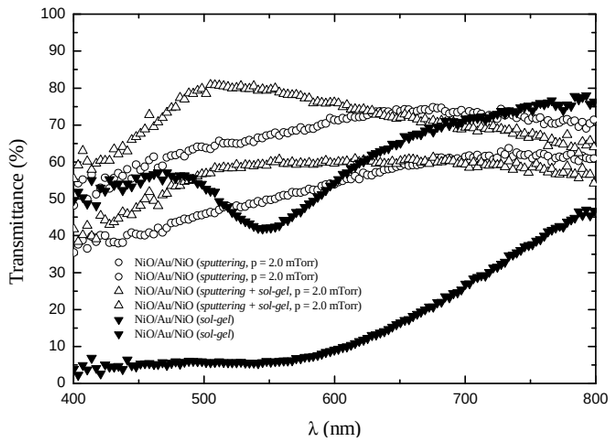

Fig. 2 - *In situ* spectral transmittance of the NiO/Au/NiO films grown by (*i*) sputtering, (ii) sputtering + sol-gel and (iii) sol-gel + dip-coating.

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