Optical properties of ZnO nanocrystallites embedded in a gold-oxide matrix

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Thin films having ZnO nanocrystallites, with a minimum average size of 2.2 nm, embedded in an amorphous gold oxide matrix have been investigated. These structures do not present a blue-shift of the absorption spectra relative to those corresponding to large ZnO crystallites, a shift which would be expectable for this range of particle size. It was found that the hydrated gold oxide has a much narrower energy gap than ZnO and does not create quantum wells in the ZnO crystallite region. The Raman spectra present only the confined vibration modes of ZnO. These peculiarities of the mixed system were analyzed by means of an adequate energy band diagram. A Raman resonant effect, determined by interface transitions, has also been detected.

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The investigation of the optical properties of elemental amorphous semiconductors by Professor Grigorovici and his co-workers revealed their most important peculiarities [1], [2]. It was evidenced the presence of an absorption edge corresponding to an optically defined “energy gap”. This is not defined so sharply as in crystalline materials and therefore, in time, different methods were developed for its determination [3].

In the last years the interest is focused on other disordered systems, the nanoparticles embedded in an amorphous matrix, which present interesting optical properties. Thus, a blue-shift in light absorption, determined by a quantum size effect, was observed in many semiconductor nanocrystalline systems. It is a very impressive effect in narrow-band semiconductor compounds like PbSe where the shift, for a 3.5 nm nanoparticles, is three times larger than the energy gap value [4]. It is an important effect also in large-gap systems like ZnO where the blue-shift is observed for both free nanoparticles and those embedded in a silica matrix [5]. The SiO$_2$ insulator has a large energy gap and small affinity value, thus creating deep quantum wells in the ZnO region.

Here we present an other system, that of ZnO nanoparticles embedded in a gold-oxide matrix. This disordered material proved to have a smaller “energy gap” than that of ZnO and the system does not show a blue-shift of the spectra relative to those of large ZnO crystallites.

Thin films containing nanocrystallites have been obtained by reactive r-f magnetron sputtering in pure O$_2$ using Zn and Au targets. The thickness of the deposited layers was about 1 µm. The variation of the gold concentration in the deposited layer was achieved by moving the gold target further away from the center of the erosion area of the Zn target. The structural analysis [6], shows that the films deposited without gold are well crystallized in a wurtzite lattice. If the gold concentration increases the size of the crystallites decreases drastically. However their hexagonal structure corresponding to ZnO lattice is preserved as it was revealed by selected area electron diffraction (SAED), X-ray diffraction (XRD) and high-resolution electron microscopy (HREM). On the other hand all these methods associated with Mössbauer spectroscopy indicate that there is no metallic Au, that there are no metallic bonds such as Au-Au or Au-Zn and that the real bond is that corresponding to a Au$^{3+}$ ion. Corroborating these results with those obtained by Elastic Recoil Detection Analysis (ERDA) we concluded that the gold is incorporated mainly as an amorphous hydrated gold oxide such as Au$_2$O$_3$.xH$_2$O with value of x around 2.7 [6]. However some Au atoms can enter as interstitials in the compact hexagonal lattice of ZnO. Taking into account all these aspects we concluded that at low gold concentration the ZnO crystallites coexist with islands of hydrated gold oxide. The further increase of the gold concentration hinders the crystallites growth and for Au versus Zn ratios larger than 0.5 the ZnO crystallites are completely covered by a hydrated gold oxide mantle. The ZnO crystallite average size for different Au/Zn ratios is presented in Table 1.

<table>
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<th>Table 1. Film characteristics.</th>
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$^a$ determined by Rutherford back-scattering
$^b$ determined by deconvolution of XRD profiles
The small crystallite size for films 4 and 5 can be also determined directly from HREM images [6], since they show well-defined nanocrystalline grains with plane distances corresponding to the wurtzite structure of ZnO. Fig. 1 presents a chart of the crystallite size distribution for film nr. 4. The average value determined from the HREM image is 2.8 nm. This is very close to the value of 3.0 nm found by the X-ray method.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{particle_size_distribution.png}
\caption{The particle size distribution in Film nr. 4.}
\end{figure}

We can also evaluate the mean distances between the ZnO crystallites for the samples 4 and 5 that have crystallites completely covered with gold oxide. Thus, supposing an uniform distribution of the gold oxide around the crystallites and using the data of Table 1, the known values of bulk densities for both zinc oxide [7] and gold oxide [8] and considering roughly that the mean distances between crystallites are twice the thickness of the gold oxide, we obtained that these mean values are 0.76 nm and 0.84 nm for films number 4 and 5 respectively.

The optical absorption was recorded using a Cary 17D infrared-visible spectrophotometer. The absorption spectra of some investigated films are presented in Fig. 2.

\begin{figure}[h]
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\includegraphics[width=0.5\textwidth]{absorption_spectra.png}
\caption{Absorption spectra of some investigated films. The numbers that labels the curves correspond to the film numbers in Table 1.}
\end{figure}

The shapes of the absorption curves corresponding to non-covered ZnO crystallites are nearly identical with those of bulk ZnO. The absorption coefficient \( \alpha \) is determined by a “direct” transition and from an \( (\alpha E)^2 \) vs. photon energy \( E \) representation [9], a value of 3.20 eV for the ZnO energy gap was found and this is indeed the room temperature value of bulk ZnO gap.

It is interesting that the absorption curves for covered ZnO crystallites (Films 4 and 5) do not present any blue-shift relative to the large crystallites ZnO spectra, even that the crystallite size is very small. Contrary, they are situated at the “red-side” of the spectra of non-covered crystallite sample. In this region they present an “Urbach tail”. This exponential tail ends at about 3 eV, which is very close to the ZnO energy gap.

On the other hand we prepared and characterized a pure hydrated gold oxide film, too. Its absorption spectrum is also presented in Fig. 2. This amorphous material has also a long exponential tail. However it is situated entirely in a much lower energy range than that corresponding to the films having ZnO crystallites. As we outlined above it is very difficult to determine the energy gap of an amorphous material. A crude procedure [3] is to take as an “energy gap” the “knee” value, i.e. the energy value for which the absorption curve ends its exponential behavior. In our case this happens at about 1.6 eV. This “energy gap” value is, of course, much lower than that of ZnO gap.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{energy_band_diagram.png}
\caption{Energy band diagram of the ZnO-Au\textsubscript{2}O\textsubscript{3}.xH\textsubscript{2}O system. The hydrated gold oxide is labeled as Au\textsubscript{2}O\textsubscript{3}.}
\end{figure}

In the absence of data concerning the amorphous gold oxide affinity but knowing that its energy gap value is much lower than that of ZnO, a possible energy diagram of ZnO nanocrystallites covered by gold oxide is presented in Fig. 3. This diagram looks like a type I super lattice one [9]. However in our case it hases random widths corresponding to each region and it is dispersed in all directions. Taking into account the very narrow dimension of the gold oxide separating layers it would be expected that the most energy levels are situated in the upper part of the well. The depth of these levels varies randomly because the spatial width of the gold oxide wells varies randomly. Therefore a tail of states is formed below the upper limit of the well as it happens in an amorphous material.

Returning to the behavior of the absorption spectra of the ZnO nanocrystallites that are covered by amorphous gold oxide layers (curves 4 and 5 in Fig. 2) we observe from Fig. 3 that the ZnO nanoparticles have no quantum wells. Therefore they would not present any blue-shift in absorption spectra. On the other hand the light absorption on the tail states of the narrow gold oxide quantum wells...
will determine a tail in the absorption spectra of these samples. However only few of these tail states extended far from the upper limit of the well. Therefore the main variation of the absorption range will be situated near the value of the energy gap of ZnO and far from the “energy gap” of the amorphous gold oxide (much lower than that of ZnO) as we can indeed observe on the experimental spectra. We can thus consider that we have to do here with a “blue-shift” of the gold oxide spectra up to the ZnO gap instead of a shift corresponding to ZnO. This behavior could be compared with the spectra of ZnO nanoparticles embedded in a SiO\(_2\) matrix [4]. In this latter case the silicon dioxide has a much larger gap than ZnO so that deep wells are formed in the zinc oxide region that determines a blue shift of the ZnO absorption spectra.

The Raman spectra of these films were also measured in a standard backscattering geometry. Two sources of excitation were used: the 488 nm line of an Ar laser and the 632.8 nm one of a He-Ne laser. Fig. 4 shows the Raman spectra obtained by excitation with the 488 nm line.

![Fig. 4. Raman spectra obtained by excitation with the 488 nm line of an Ar laser. The labels on the curves correspond to the film numbers in Table 1. The curves are shifted vertically for clarity.](image1)

The Raman lines observed are that corresponding to a ZnO lattice. Thus, it can be seen the transverse \(E_2\) line at 437 cm\(^{-1}\), the broad band from 540 to 670 cm\(^{-1}\) in which are involved the \(A_1(LO)\) line, the \(E_1(LO)\) line and other multi-phonon lines, between them being the two \(E_2\) lines. There are also other multi-phonon bands at 750-820 cm\(^{-1}\) and 1050-1150 cm\(^{-1}\). However, all these bands are usually observed also in single-crystal samples [10,11].

We can see that the Raman spectra of the films in which the ZnO nanocrystallites are embedded in a gold oxide matrix (films 4 and 5) are similar with those of large crystallites ZnO film (Film nr. 1). Only a small broadening of the band around 600 cm\(^{-1}\) can be observed. Therefore in these mixed films we have observed only the well known ZnO Raman lines and we have not found any specific vibration modes connected with gold oxide. However we have not detected them even in the pure gold oxide films either. It is interesting to observe that a similar behavior is usually found in superlattice structures in which the confined optic modes exist in one of the component but not in the other [9]. Therefore there are no “mixed” frequencies.

Interesting aspects was found also in the Raman spectra of samples excited with the red line of the He-Ne laser (Fig. 5). The Raman spectrum of the pure ZnO film shows again the specific bands for this material but with lower amplitudes. This is a normal behavior for a lower exciting frequency. If the concentration of gold oxide increases, the left multi-phonon band is distorted by the development of a maximum centered approximately at 640 cm\(^{-1}\). For the films nr. 4 and 5, having the smallest nanocrystallites embedded in gold oxide, the amplitude of this maximum increased drastically indicating a resonant effect.

![Fig. 5. Raman spectra obtained with an excitation line of 632.8 nm of a He-Ne laser. The labels on the curves correspond to the film numbers in Table 1. The curves are shifted vertically for clarity.](image2)

This resonance does not affect the pure ZnO film and therefore it must be connected with the interface between the ZnO crystallites and the gold oxide matrix. It may be a surface enhanced Raman scattering effect (SERS). However, the usual electro-magnetic (em) model [12], is not adequate for this system. Indeed, it involves the presence of a rough metallic surface that allows the presence of an oscillating plasma. We have mentioned above that we have not found any traces of gold clusters by different method of investigations. Therefore we must conclude that we have to deal here with a Raman resonance that involves resonant transitions between states at the interface between the ZnO crystallites and the gold oxide coverage including a charge transfer process [13].

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References


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