Gold clusters on WO$_3$ nanoneedles grown via AACVD: XPS and TEM studies

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ABSTRACT

We have prepared tungsten oxide films decorated with gold particles on Si substrates by aerosol assisted chemical vapor deposition (AACVD) and characterized them using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). SEM shows that the films are composed of needle-like structures and TEM shows that both the needles and the gold particles are crystalline. XPS indicates the presence of oxygen vacancies, i.e. the films are WO$_3$-$x$, and hence the deposited material is composed of semiconducting nanostructures and that the interaction between the gold particles and the WO$_3$ needles surface is weak. The synthesis of semiconducting tungsten oxide nanostructures decorated with metal particles represents an important step towards the development of sensing devices with optimal properties.

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1. Introduction

Transition metal oxides have electronic and chemical properties that can be fine tuned during their synthesis; this flexibility makes them outstanding candidates for a wide range of applications [1–6]. In this context, tungsten oxide films have already proved their applicability as active material in diverse applications including electrochromic devices and gas sensing, and much effort has been directed at optimizing the performance of tungsten oxide films in sensing devices [6–16]. Compared to the traditional 3D, thin films tungsten oxide low-dimensional structures exhibit higher surface to volume ratio and particular phase structures that attract great interest in gas sensing applications [17–21]. Additionally, low-dimensional metal oxides are often single crystalline nanostructures with well-defined catalytic properties, which helps in gaining insight into the gas sensing mechanisms of such nanostructures. Consequently their synthesis and characterization has been the focus of much research in recent years. Several synthesis methods of tungsten oxide nanostructured films have been reported [22–26], among them aerosol assisted chemical vapor deposition (AACVD) has been shown to produce films formed by needle-like nanostructures with remarkable sensing properties significantly exceeding those of commercially available metal oxide sensors [27].

Although, pure metal oxide active layer sensors can have high sensitivity, they have typically poor selectivity. To overcome this drawback noble metals that act as catalysts can be added to the metal oxide active layer [15,28–30]. Several methods have been used to add catalytic active dopants to the sensing active material, in some of them the dopants are inserted within the bulk of the sensing active material and in others, often used, the dopants are deposited on the top of the sensing layer [17]. In this context, gold has been used regularly as an electronic or chemical sensitizer in tungsten oxide films for gas sensing. Yamazoe and co-workers showed that loading tungsten oxide films at 0.8% wt. with Au resulted in a highly enhanced sensitivity to ammonia vapors [31]. Gold loading has also been reported beneficial for enhancing sensitivity to nitrogen oxides [32] or hydrogen sulphide [28]. Haruta and co-workers reported that in the case of Au–WO$_3$ composite films, the combination of Au made such films sensitive mainly at the plasmon absorption region around visible wavelengths, which enhanced the optical detection of H$_2$ [33]. Recently, we reported the co-growth using AACVD of preformed gold nanoparticles and gold precursors into dense-like MOX film [34,35]. These methods lead to
the growth, in a single step, of metal oxide nanoneedles having their surface decorated with gold nanoparticles.

Herein, we report on the characterization of Au-decorated WO$_3$ needle like nanostructures deposited using AACVD. The WO$_3$ films and the nature of the Au/WO$_3$ interface were characterized using X-ray photoelectron spectroscopy (XPS), transmission (TEM) and scanning electron (SEM) microscopy. The nature of the Au/WO$_3$ interface strongly impacts in the electrical transparency of the Au/WO$_3$.

2. Experimental

WO$_3$ and Au/WO$_3$ nanoneedles were grown on Si substrates by Aerosol Assisted Chemical Vapor Deposition (AACVD) at 500 °C and 450 °C respectively, details have been reported elsewhere [27]. Briefly, tungsten hexaphenoxide [W(OPh)$_6$] and hydrogen tetrachloroaurate (III) [HAuCl$_4$], were used as precursor materials. Precursors, in the form of an aerosol, were carried into the CVD reactor by a nitrogen flow.

The chemical composition of the samples was investigated using X-ray photoelectron spectroscopy (XPS), VERSAPROBE PHI 5000 from Physical Electronics, equipped with a Monochromatic Al K$_\alpha$ X-Ray. The energy resolution was 0.6 eV. For the compensation of built up charge on the sample surface during the measurements, a dual beam charge neutralization composed of an electron gun (−1 eV) and the Argon Ion gun (≤10 eV) was used. All binding energies were calibrated to the C 1s peak at 284.3 eV. To support the interpretation of the XPS spectra, three standard samples were used. As reported elsewhere [27], three doublets were used to reproduce the W 4f spectrum, 3 doublets were used to fit the W 4f core level and one Gaussian for the W 5p orbit doublet of W 4f.

To observe the morphology of the WO$_3$ nanoneedles a FEI Nova 200 Nanolab Dual Beam SEM/FIB system was used while the microstructure of the WO$_3$ nanoneedles was studied using a JEOL JEM-2100 transmission electron microscope (TEM).

3. Results and discussion

Fig. 1 shows SEM images of the WO$_3$ film grown on the Si substrate. A high density of non-aligned needles was observed both in the WO$_3$ and Au/WO$_3$ samples with similar morphological features. Further information about the structure of the nanoneedles was obtained by TEM (Fig. 2). The diameter of WO$_3$ nanoneedles was found in the range of 15–60 nm. The nanoneedles are monophasic; clear lattice fringes can be observed in two insets in Fig. 2 with interplanar spacing of 0.35–0.37 nm consistent with an internal order of the WO$_3$ nanoneedles in the [001] (0.5d = 0.3650 nm) or [020] (0.5d = 0.3770 nm) directions. The upper inset of Fig. 2, shows a typical high resolution image of Au nanoparticles, it can be observed a family of planes with lattice spacing of 2.4 Å, corresponding to (111) planes. In the inset of Fig. 2, we can observe that the atomic planes under the particles are not affected by the presence of the particle suggesting a weak interaction between particle and the surface of the WO$_3$. The nanoneedle surface is homogeneously covered with well-dispersed quasi-spherical gold nanoparticles with diameters between 9 and 25 nm (Fig. 3).

To study the nature of the chemical bonding at the interface Au/ WO$_3$ we used XPS. The analysis of both core and valence (bonding electrons) electronic states gives information on the chemical nature of the samples. The fundamental phenomenon underlying the XPS is the photoelectric effect that describes the ejection of electrons from a surface when photons impinge upon it. The kinetic energy (or binding energy) of the ejected electron is characteristic of each element and its chemical state. The W 4f and W 5p$_{3/2}$ core level spectra were recorded using XPS on a M4000 W4f1/2 powder sample (Fig. 4a) on WO$_3$ nanoneedles grown on Si (Fig. 4b) and the co-deposited Au nanoparticles and WO$_3$ nanoneedles grown on Si (Fig. 4c). According to the reported procedure for fitting the spin-orbit doublet of W 4f [36–39], to reproduce the nanoneedles spectra, 3 doublets were used to fit the W 4f core level and one Gaussian for the W 5p$_{3/2}$. The FWHM of the W 4f peaks recorded on the WO$_3$ needles and Au/WO$_3$ (Fig. 4b and c respectively) were larger than the ones recorded on the reference powder. The main doublet (W 4f$_{1/2}$) is centered at 35.4 eV, it is generated by photoelectrons emitted from W atoms with oxidation state +6 (WO$_3$). The second doublet (W 4f$_{1/2}$) centered at 34.4 eV can be attributed to photoelectrons emitted from tungsten atoms near oxygen vacancies, where the oxidation state of W is lower than +6 (substoichiometric WO$_{3-x}$). This component has a weak contribution in the spectrum recorded on the WO$_3$ standard (~9%, Fig. 4a), conversely on the spectrum recorded on the WO$_3$ nanoneedles (Fig. 4b and c) the area under this component correspond to 27% of the total W 4f peak suggesting a higher concentration of oxygen vacancies. The third doublet used to reproduce the W 4f core level is centered at 36.2 eV − the origin of this component was reported to be associated to local variations in the vacuum-level energy ($E_{dl}$) caused by surface defects [40]. Photoelectrons emitted from the same chemical environment will experience different values of $E_{dl}$ in traversing the surface, and will arrive at the analyzer with a different kinetic energy. The contribution of surface defects can be expected to be quantitatively important in an XPS spectrum recorded using energy of excitation in the order of the used one (1486.4 eV). The third doublet has the same contribution to the total intensity of the W 4f spectrum recorded on the WO$_3$ nanoneedles and Au/WO$_3$ nanoneedles suggesting a weak interaction of the Au clusters with the WO$_3$ needles. It has been shown that, in some oxides doped with metal atoms, under certain conditions the metal atoms can diffuse and localize preferentially at defect sites such as oxygen vacancies [40]. If this is the case, it is expected that Au particles nucleate on these sites, thus the photoelectrons emitted from W atoms beneath the gold particles would experience inelastic losses when passing through the metal particle, and thus no longer contribute to the W 4f peak. Therefore, the absence of a measurable reduction in the relative intensity of the component at 36.2 eV suggests that the gold particle distribution is not mediated by the presence of defects at the nanoneedles surface. Further studies will be performed aiming at determining...
the mechanism that causes the intrinsic spatial particle distribution at the WO₃ needle surface in the AACVD synthesis. The Au 4f core level spectrum recorded on the Au/WO₃ at 84 eV (Fig. 5) is similar to the one reported for the Au crystal indicating that the co-deposited Au particles are in the metallic state [41]. The absence of new structures in the Au 4f spectrum testifies our assertion of weak interaction at the gold/WO₃ interface.

In Fig. 6 the O 1s peaks are shown. Besides the small chemical shift from the powder reference sample to the pristine WO₃ nanoneedles (also observed in the W 4f peak), a second component of oxygen centered at 533 eV is present in the case where Au nanoparticles are co-deposited. Due to the large area of that component (1/3 of the main peak) and the lack of additional structures on the W 4f core level that could suggest another oxidation state for the tungsten, the origin of this peak can be assigned to contamination on the sample. In fact, the carbon concentration in the Au/WO₃ samples was found to be higher than on the WO₃ samples suggesting the presence of organic fragments probably due to the lower temperature used during the synthesis.

The valence electronic states of the samples can be seen in Fig. 7. The WO₃ reference sample (blue line) and WO₃ nanoneedles (black line) spectra show similar features. Covalent bonding interactions transform the O 2p and the metal d-orbitals into bonding and antibonding orbitals of mixed atomic character. Reported, calculations of the valence band density of states (VB-DOS) for monoclinic WO₃ assigned the peak located at about 4.1 eV to an O 2p-derived band while the peak located at about 6 eV corresponds to a hybridized ‘W 5d–O 2p’ band [42,43]. The rapid onset of the VB spectrum at about 3.0 eV can be assigned to the top of the valence band, and the well-defined structure near the Fermi level (Eₜ = 0) is associated to W 5d in-gap states, whose filling is due to the
presence of oxygen vacancies [37]. In stoichiometric WO$_3$ samples, the 5d-derived states near the gap are empty and no states are observable at the Fermi level [37,40,42,43]. However, if there are oxygen vacancies or lower valence WO$_x$ ($x < 2$) states as well as W (0) not all the ‘5d-electrons’ can be transferred and the 5d-derived states near the gap are populated. The presence of a structure near the Fermi level (not expected for an insulator) suggests that there are sub-oxides or oxygen vacancies, which support our assertion of the component at binding energy equal to 36.2 eV to the presence of defects (black component in Fig. 6). Comparing the spectra of the valence band recorded on the standard samples and on the pristine WO$_3$ needles, it can be seen that the structure at the Fermi level is more pronounced in the needles spectrum confirming our assertion that the needles have more oxygen vacancies. The loss of oxygen atoms leaves behind extra electrons resulting in a material behaving as n-type semiconductor. The presence of tungsten oxide sub-oxides and surface defects (i.e. oxygen vacancies) is of interest for tungsten oxide based chemical sensors. The baseline conductance of semiconducting WO$_3$ nanoneedles will depend on the oxygen species adsorbed at their surface defects [10–12]. The presence of oxidizing or reducing species that alter the equilibrium concentration of oxygen adsorbates can be monitored via the change in electrical conductance experienced by the nanoneedles [27].

The valence band spectrum recorded on WO$_3$ needles decorated with gold particles presents a new structure peaking at 6.0 eV and, another at 1.4 eV. The gold valence band is formed by a 5d band, characterized by the 5d doublet with weighted centers at 6.35 eV and 3.55 eV and a wide “s–p” band formed mainly by 6s and 6p electrons (partially hybridized with 5d-orbitals), localized above the 5d states and below the Fermi level [41]. Thus the new observed features can be associated with photoelectrons emitted from gold atoms forming the clusters. The 5d spin orbit splitting reflects the number of Au nearest neighbors surrounding a gold atom and consequently the strength of the Au–Au interactions. Thus, the observed 5d spin–orbit splitting supports our assertion that the clusters are in the metallic state.

4. Conclusions

In summary, using aerosol assisted chemical vapor deposition WO$_3$ nanoneedles and Au-decorated WO$_3$ nanoneedles can be synthesized with high yields. Both, WO$_3$ and Au-decorated WO$_3$ nanoneedles are single crystalline and show oxygen vacancies indicating a semiconducting behavior. Well-dispersed Au nanoparticles homogeneously cover the WO$_3$ surface. The absence of additional structures in the Au 4f peak suggests a weak interaction at the Au/WO$_3$ interface. The well-dispersed Au nanoparticles can play an important role for sensitizing the tungsten oxide nanoneedles via a spill-over effect. The obtained nanomaterial represents an excellent model for both experimentally and theoretically studying the interaction between metal oxides nanostructures and gas molecules in view of gaining more insight in the mechanisms of gas sensing.

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