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Charge Transfer in Amorphous Colored WO_3 Films Observed by X-Ray Photoelectron Spectroscopy

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X-ray photoemission spectra of W core levels and valence band in transparent and *in situ* uv-colored amorphous WO_3 films show that coloration is related to the existence of occupied electronic W^{5+} states situated ~ 2 eV above the valence band and localized on some tungsten sites. It is shown that x-ray photoelectron spectroscopy and optical data are understood if one considers the formation of a hydrogen-tungsten-bronze–like compound during uv irradiation.

Amorphous tungsten oxide thin films prepared by thermal evaporation under vacuum of WO_3 powder exhibit two stable states—the first one is transparent and highly resistive and the second one is blue and less resistive. Virgin layers are transparent. The blue coloration arises from a broad absorption band with a maximum at 900 nm (1.38 eV) and can be induced either by uv irradiation[1] ($h\nu > 3.4$ eV), by application of an electrical field[1] ($E \sim 10^4$ V/cm), or by proton injection.[2,3] Different models have been put forward on the origin of the absorption band.[1-3] In the earlier model, Deb[1] suggests *F*-center–like absorption between the fundamental and the excited states of an electron trapped in an oxygen vacancy. Later models[2,3] attribute the coloration to the existence of a hydrogen-tungsten-bronze H_xWO_3 formed by proton injection; Faughnan, Crandall, and McGee[2] suggest intervalence electron transfer between W^{5+} and W^{6+} valence states as a microscopic mechanism.

From optical measurements, the concentration of optical centers amounts to about 5×10^{20} and 10^{22} cm^{-3}, respectively, for uv coloration[1-4] and proton injection[2]; thus, x-ray photoelectron spectroscopy (XPS) demonstrates sufficient sensitivity to investigate the electronic structure of the films in the virgin and colored states and to give information on the origin of the absorption band and on the coloration mechanism. On the other hand, these results on amorphous material can be compared with those of crystalline bronzes Na_xWO_3[5] since host-matrix effects are expected to be dominant in these compounds.[6] Core level measurements allow detection of charge transfer whereas valence band spectra display a view of the density of occupied states. Hersh, Kramer, and McGee[3] have recently measured WO_3 films colored by proton injection, and Rabalais, Cotton, and Gazman,[7] transparent and colored amorphous MoO_3 films. They have observed the appearance of electronic states near the Fermi energy but did not detect any modification of the core levels. Since the samples have probably been transferred through the atmosphere before entering the spectrometer, no firm conclusion can be drawn from their experiments.

In this Letter we present the first XPS results for tungsten oxide thin films evaporated and uv-colored, both *in situ*. The data show firm evidence that coloration is related to the growth of electronic states arising ~2 eV above the main valence band and localized on some tungsten atomic sites giving rise to W^{5+} valence states. These results reject the occurence of the absorption band from increasing electron trapping in oxygen vacancies ("color center" model[1]); on the contrary, they support the small-polaron model emerging from electrical and optical measurements[4] or intervalence electron transfer[2] between W^{5+} and W^{6+}. The comparison with XPS data from Na_xWO_3 gives striking evidence for electron localization induced by the amorphous state.

It is imperative to prepare the samples *in situ* since films transferred through the atmosphere are covered by a contamination overlayer containing stoichiometric WO_3 and carbonaceous products. Samples were prepared inside the preparation chamber of the spectrometer by vacuum evaporation of analytical grade WO_3 powder from a tantalum boat. The base pressure was 10^{-7} Torr and rose to 10^{-5} Torr during evaporation. Characterization of evaporated films prepared under the same conditions have been systematically made.[8] The stoichiometry was measured by proton backscattering using as standards fully oxidized evaporated films and layers sputtered from a WO_3 target in a pure oxygen atmosphere. Absolute values of hydrogen content were determined from the count of α particles emitted from the nuclear reaction $B^{11} + H \rightarrow \alpha + B^{8*}$. Stoichiometry is nearly constant (O/W ~ 2.7) but hydrogen content varies ($H_xWO_{2.7}$ with $0.2 < x < 0.5$) from one layer to another.[8] These values remain unchanged after uv insolation. The hydrogen atoms come from water contamination of the WO_3 powder and trapping of the residual vapor during evaporation.

XPS spectra were obtained with a Hewlett Packard 5950 A spectrometer using monochromatized Al $K\alpha$ radiation. The overall instrumental resolution was 0.55 eV. The films were deposited onto glass substrates (for further optical measurements) or metal ones. In this latter case no charging effect was detected during measurements. In Fig. 1, curves a and a' display the XPS spectrum of the W $4f$ core-level doublet and the valence-band spectrum for crystallized WO_3 obtained by thermal oxidation of tungsten. In Fig. 1, curves b and b' are for virgin amorphous films; W $4f$ widths are 0.2 eV larger and, in addition, below the component relative to the W^{6+} formal oxidation state appears a low-intensity component located ~1 eV toward lower binding energy which is attributed to the W^{5+} state. It is difficult to give the exact W^{5+}/W^{6+} concentration ratio because x-ray irradiation produces analogous but very much attenuated effects as uv irradiation. In the hypothesis of neutral hydrogen, doubly negative oxygen, and electron localization only on tungsten atoms, the W^{5+}/W^{6+} ratio (< 10%) is too small to give bulk stoichiometry, so a slight superficial oxidation might have occurred. The structure of the valence band of crystallized WO_3 is smeared out in amorphous film, and a

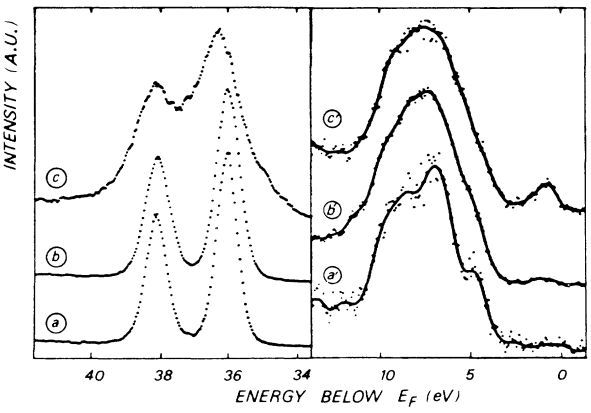

FIG. 1. Curves a and a' are W $4f$ and valence-band spectra of crystallized WO_3, b and b' are the same for transparent amorphous "WO_3" films, and c and c' for uv-colored films.

new structure with very small intensity appears ~2 eV above the valence band as well.

In Fig. 1, curves *c* and *c′* show XPS spectra after coloration of the film by *in situ* uv irradiation. A quite deep modification affects the W 4*f* lines; meanwhile the density of states near the Fermi level noticeably increases. By subtracting the W^{6+} dominant virgin spectrum from the insolated film spectrum, two other components are shown in W 4*f* peaks. The first component at 1 eV lower binding energy relative to W^{6+} levels corresponds to an increase of the concentration of W^{5+} states. The assignment of this component to W^{5+} level has been discussed previously.[8] It appears in spectra of reactively sputtered WO_x films and of samples obtained by heating a mixture of W and WO_3 powder or by Ar^+ ion-bombarded WO_3 surfaces; its 1-eV relative chemical shift is lower than the 3-eV shift corresponding to W^{4+} in WO_2.[8-9] The assignment of the second component at 1-eV higher binding energy is less obvious. It is likely that it originates from plasmon excitation. Such structures have been observed in ReO_3 and Na_xWO_3 XPS spectra[5] with energy losses of around 2.3 eV. The plasma frequency ω_p increases with the number of free (or nearly free) electrons. The value for $\hbar\omega_p$ is expected to be ~1.5 for $x=0.2$. A higher-binding-energy component also accompanies the O 1*s* level in the colored film, which may confirm this hypothesis; however, uv irradiation carries on a carbonaceous contamination which may alter also the O 1*s* signal.

Figure 2 shows the W 4*f* spectrum of colored film, resolved into four doublets corresponding to W^{6+} and W^{5+} levels with their corresponding plasmon satellites, with use of an iterative least-squares procedure. From the agreement between calculated and experimental curves we cannot rule out other contributions such as interband transitions or other many-body effects. Relative to the W^{6+} level, the energy shift for the W^{5+} is equal to 1.2 eV with the W^{5+}/W^{6+} ratio equal to 0.26, and the plasmon satellite suffers a 0.85-eV loss. Irradiation induces a structure near the Fermi level at 2 eV above the valence band, the whole spectrum being very similar to that obtained from crystalline $Na_{0.8}WO_3$[5] (Fig. 3). The structure is a bit larger here (full width at half-maximum = 1.3 eV instead of 1.15 eV).

Band-structure calculations either for WO_3, WO_{3-x}, or tungsten bronzes have not yet been published. However Mattheiss has performed the ReO_3 band calculation and it could be argued[6,11] that for the former compounds the results should be quite similar; only a difference in the Fermi level position is expected, depdnding on the number of valence electrons, with E_F around the midgap for WO_3 (empty conduction band) and around the bottom of the conduction band for ReO_3 and Na_xWO_3 (partially filled conduction band). The XPS valence-band spectrum for ReO_3[12] fits the theoretical density of states,[10] provided the Re 5*d* x-ray photoionization cross section is accounted to be ~30 times higher than the one for O 2*p*. It has been concluded that the π^* conduction band in ReO_3 is mainly of Re 5*d* character.[12] Campagna *et al.*[5] from XPS measurements of Na_xWO_3 verified similarly the essentially W 5*d* character of the conduction band, filled up by electrons provided by Na atoms which are so far fully ionized. So, in our colored films the electronic states

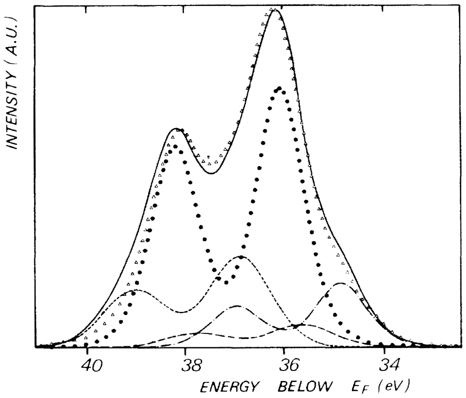

FIG. 2. Colored film W 4*f* spectrum, resolved into contributions from the W^{6+} state (· · ·), the W^{5+} state (· – ·), and their satellites, respectively, (– – –) and (— — —).

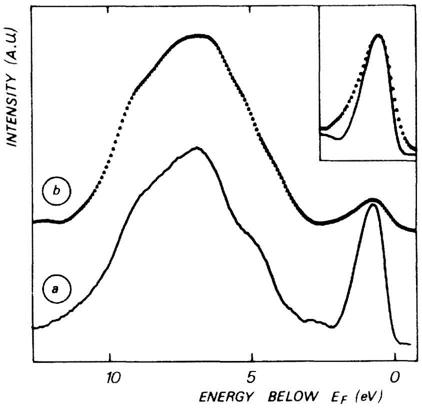

FIG. 3. Comparison of (a) valence-band XPS spectra of $Na_{0.8}WO_3$ (Ref. 5) and (b) uv-colored amorphous "WO_3" films. The inset shows the normalized conduction band of the two compounds.

near the Fermi level are also expected to have an essentially W 5d character.

Experimental results both on the core level and valence band indicate then that the absorption band in the colored state corresponds to an increase of electrons localized on tungsten sites instead of oxygen vacancies. This obliterates the "color center" model,[1] but supports the intervalence model[2] or small-polaron model[4] where the absorption band originates from electron excitation between W^{5+} and W^{6+} ions. From the comparison of the bumps in colored films and in Na_xWO_3 crystals and under the assumption that x electrons fill the band in the latter case. we deduce a number—0.3 electron per W in the colored film—in rough agreement with the W^{5+}/W^{6+} ratio of ~0.26 in core levels. If we suppose these average 0.3 electrons per W come from hydrogen and all the hydrogen are ionized in the colored state, this gives for the film $H/W = 0.3$, in agreement with characterization results $H_xWO_{2.7}$, $0.2 < x < 0.5$.

The detection of a unique W 4f doublet in Na_xWO_3[5] which continuously shifts towards lower binding energy (that means an enhancement of local electron density on all tungsten sites) with increasing Na atoms confirms delocalization of d electrons in this band, giving then metallic conductivity. On the contrary, in amorphous films they remain localized on some tungsten sites giving W^{5+} levels. This localization is confirmed by the semiconductor character of the films. These differences can be understood from the amorphous state of the films and the physical origin of the conduction band of transition-metal perovskites.[6-10] In such compounds, the bottom of the conduction band and the top of the valence band arise from hybridization of metal t_{2g} orbitals with oxygen p_π orbitals giving the metallic conductivity when they are partially filled with electrons (Na_xWO_3, ReO_3). In our amorphous films strong crystallographic distortions occur and W t_{2g} orbitals are expected to be more localized on specific atomic sites, allowing only hopping conduction between localized W^{5+} levels; meanwhile higher overlap between W e_g and O p_σ remains. Such an interpretation is supported by optical data. For a single crystal of WO_3, Dickens, Quilliam, and Whittingham[13] have found the absorption edge at 2.7 eV, which is consistent with the gap deduced from the XPS spectra of Na_xWO_3.[5] In amorphous WO_3 films, the optical absorption edge and the photocurrent threshold occur at an energy greater than 3.3 eV[4] whereas the first localized occupied states (W^{5+}) above the valence band in the colored film appear at an energy very close to the Na_xWO_3 conduction band (Fig. 3). So, in amorphous "WO_3" films, the character of the electrons in W t_{2g}, O p_π hybridized orbitals is intermediate between the two extreme cases: Delocalized (Na_xWO_3) or fully localized.

In conclusion, we have shown that coloration in amorphous tungsten oxide films is connected with an increase of localized electronic states (W^{5+}), situated ~2 eV above the valence-band edge. It might come from small polaron formation or excitation of intervalence ion transfer which seems to appear with hydrogen ionization. Localized states correspond to the conduction band in Na_xWO_3, the disorder in amorphous H_xWO_{3-x} not allowing sufficient $W(t_{2g})$-$O(p_\pi)$ overlap for electron delocalization.

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