Formation of Intermediate Bands Within the Gap of Amorphous Oxygen-deficient and Hydrogen-Doped Molybdenum and Tungsten Oxide Films

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Semiconductors exhibiting intermediate bands (IB) are a subject of intense research during last twenty years mainly because theoretical calculations have shown that single-junction solar cells build on them have a detailed balance efficiency of 62.3% compared with the 40.7% for an ordinary solar cell. Also, in recent years IB semiconductors were successfully used to modify electrodes in hybrid organic-inorganic electronic devices such as light emitting diodes and solar cells to inject and extract carriers through the IBs in the organic semiconductor.
To be useful an IB semiconductor must fulfill a few conditions. For instance, for use in solar cells the electronic transitions between valence, conduction (VB and CB, respectively) and IBs must be allowed and strong, the corresponding absorption spectra must not overlap, must fit with the spectrum of the light to be absorbed and the non-radiative recombination of IB electrons with VB holes must be low. Moreover for electrode modification applications, the IB must not act as trap for free electrons and holes within the CB and VB respectively and the IB must be several kT away from CB and VB to avoid thermal escape of IB carriers towards them thus destroying the alignment of the various levels.
Intermediate bands may also be formed in semiconducting transition metal oxides (TMOs) such as those of tungsten and of molybdenum. These oxides exhibit a rigid metal-oxygen network, which can be modified either by removing oxygen ions from the lattice (reducing them) or by intercalating various dopants (such as H, Li, Na, etc.) or both, without destroying their basic electronic structure. Moreover, it was shown that by controlling the stoichiometry or/and the doping, IBs may be formed at the desired energy levels. Hence, TMOs with the appropriate oxygen stoichiometry and doping level may be tailored with electronic structures "on demand" so as to be useful in facilitating charge transport at interfaces by aligning the various levels of semiconductors and of metals, therefore are potentially useful in applications related to charge injection in semiconductor devices and energy photo-generation and harvesting. In recent years our group has used successfully oxygen sub-stoichiometric and/or hydrogen doped tungsten and molybdenum oxide films for the engineering of electrodes in organic light-emitting diodes and solar cells [1, 2].
This work deals with the IBs in amorphous molybdenum and tungsten oxide films with various degrees of oxygen stoichiometry and hydrogenation. When these oxides are reduced by losing oxygen and/or by introducing hydrogen within the Metal-Oxygen lattice, energy states appear within their forbidden gaps, which above a certain concentration become bands while the oxides retain their semiconducting character. Optical properties, such as Fourrier transform infrared (FTIR) spectroscopy, spectroscopic ellipsometry (SE) and photoluminescence (PL) spectroscopy are used to probe the composition and the electronic structure of deposited samples near and within the energy band gap and schematic energy diagrams are proposed for both oxides.

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References

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Figures

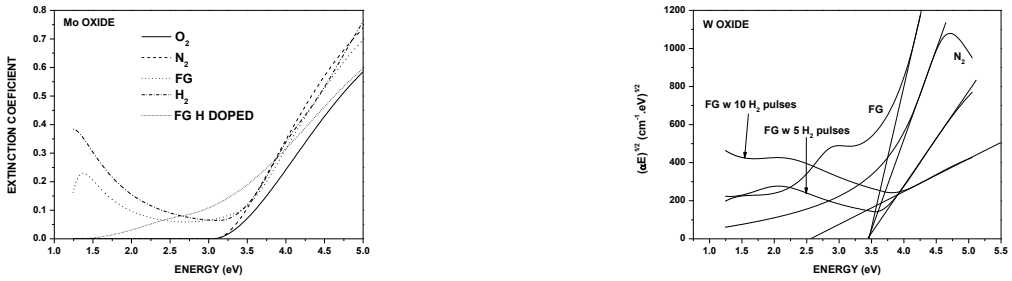

Figure 1. (Left) Variation of the extinction coefficient (imaginary part of refractive index) with photon energy for five molybdenum oxide samples grown in: O_2, N_2, FG, and H_2 environments and in FG environment and doped with protons. (Right) Tauc's plots for tungsten oxide samples grown in: N_2, FG, environments and in FG environment with simultaneous pulsed injection of H_2. It is observed that all films exhibit a band gap and IBs.

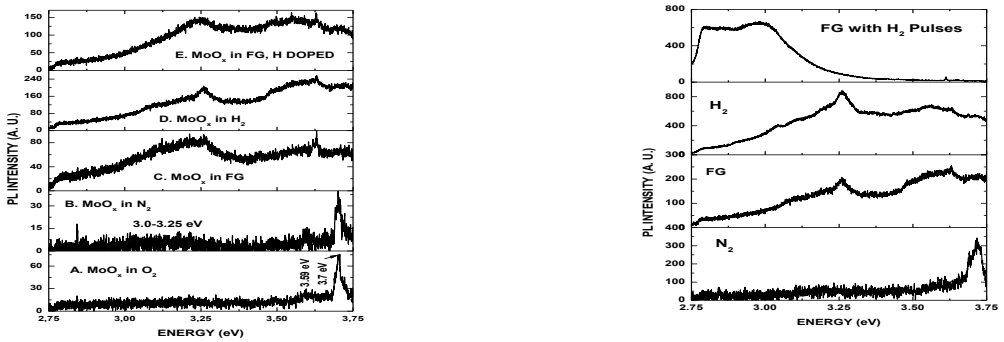

Figure 2 Photoluminescence spectra taken with excitation radiation of 3.81 eV on five molybdenum oxide samples (left) grown in: O_2 (Panel A), N_2 (Panel B), FG (Panel C), and H_2 (Panel D) environments and in FG environment and doped with protons (Panel E). The corresponding PL spectra for tungsten oxide samples are also shown (Right).

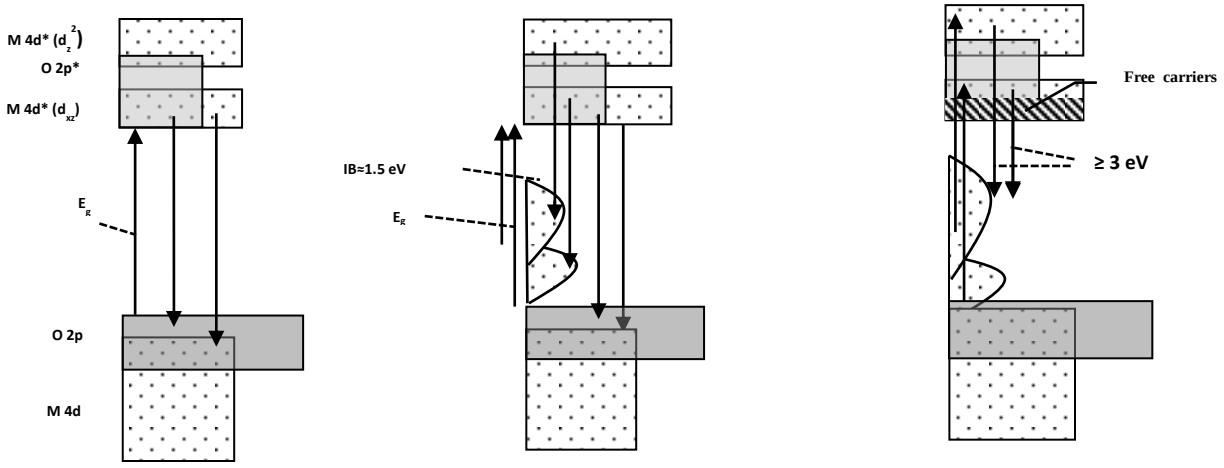

Figure 3. The proposed electronic structure of Mo and W oxide in the stoichiometric and undoped form (left) when oxygen defective and H doped they exhibit IBs (centre). For highly doped and/or oxygen deficient tungsten oxide free carriers appear at the bottom of the conduction band quenching the PL emission above 3 eV (see Fig. 3). The DOS is represented on the horizontal axis (not in scale) and the energy on the vertical. Arrows pointing upwards correspond to optical absorption (Fig. 1) while those pointing downwards to PL emission (Fig. 3) electronic transitions.