

Photochromic coloration of WO₃ with visible light

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Thin amorphous films of tungsten oxide (WO₃) are well known to change their optical absorption behavior upon light exposure, usually referred to as photochromic effect. Since the formation of color centers is closely related to the optical creation of electron-hole pairs the sensitivity of the photochromic effect in WO₃ is limited to energies above its band-gap energy of 3.25 eV, corresponding to the near-ultraviolet range. We will demonstrate that in case of a thin cadmium sulfide (CdS) layer underneath the tungsten oxide film the sensitivity of photochromism is shifted into the visible range. This result is interpreted in terms of charge carrier injection from the CdS into the WO₃. Apart from a more detailed understanding of the photochromic effect this may have also relevance for technical applications. © 1996 American Institute of Physics. [S0003-6951(96)01420-9]

Due to the high potential of large area optical devices capable to be switched between a transparent and a strong absorptive state there is a large research activity within the last two decades regarding transition metal oxides.¹⁻³ One of the most promising candidates is tungsten oxide, often discussed in the context of "smart windows" in order to control the solar input of buildings or with respect to large area displays.^{2,4} For most of these purposes the so-called electrochromic effect is used, where coloration and bleaching of tungsten oxide is caused by an electrochemical reaction. Much less attention has been paid so far to the light-induced coloration of WO₃, i.e., photochromism, where an identical absorption band is formed upon irradiating bare tungsten oxide thin films with light.^{1,5} Taking into account that the photochromic coloration can be made completely reversible by exposing the sample to oxygen gas,⁶ the basic requirements for technical applications like erasable optical storage devices are met by the photochromic effect. However, since the formation of color centers in WO₃ requires irradiation in the near-ultraviolet range^{1,6} where no compact light sources such as laser diodes are available at the moment, this may impede the development of integrated storage devices based on WO₃ considerably.

In this letter we will demonstrate that the spectral sensitivity of photochromism in tungsten oxide can be shifted from the near-UV into the visible range by the use of a thin cadmium sulfide interlayer between the substrate and the WO₃ film. In addition to a more detailed understanding of the coloration mechanism, this result may also have relevance for the above-mentioned applications.

It has already been demonstrated that the photochromic effect in tungsten oxide is intimately connected to optically excited electron (e^-) hole (h^+) pairs which can decompose water being incorporated in WO₃ to a considerable amount.⁶ The light-induced decomposition of H₂O can be written as:^{7,8}



which describes the creation of protons (H⁺) and metastable oxygen radicals (O). The protons together with the optically

excited electrons finally lead to the formation of the colored tungsten bronze HWO₃, whereas the oxygen is assumed to occupy vacancy sites inside the sample or escape (in molecular form) into the ambient atmosphere, respectively.⁶ Due to the high band-gap energy of WO₃ [3.25 eV (Ref. 1)], however, excitation of electron-hole pairs and subsequent coloration is limited to the near-ultraviolet range. The aim of this letter is to demonstrate that coloration can be already observed at considerably lower energy of the incident photon quanta if the tungsten oxide layer is in contact with a thin CdS film.

Thin films of CdS were deposited on glass substrates 10×10 mm² by a chemical bath deposition (CBD) process at a temperature of 65 °C. For details concerning the preparation process we refer to the literature.⁹⁻¹¹ The film thickness used in our experiments was determined to be about 70 nm. Figure 1 shows the absorption coefficient α of the CdS layer as a function of the incident photon energy $h\nu$ in a $(\alpha h\nu)^2$ vs $h\nu$ plot.¹² The linear increase towards higher energies clearly demonstrates a direct interband transition as it is also found for single crystals of CdS. The deviations from a straight line below 2.6 eV can be ascribed to competing noninterband absorption processes, possibly being due to impurities or internal stress. From a linear extrapolation of the

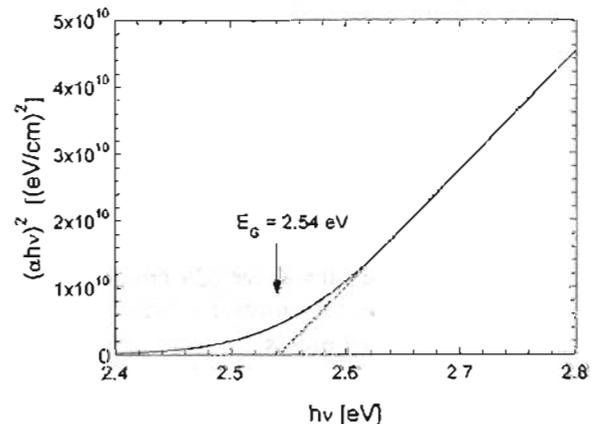


FIG. 1. Dependence of $(\alpha h\nu)^2$ for a 70 nm thick CdS film on the photon energy near the fundamental absorption edge. From the abscissa intercept of the dotted line the band-gap energy is determined to be 2.54 eV (Ref. 12).

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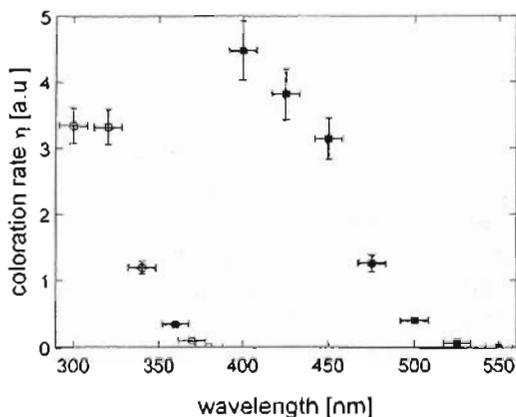


FIG. 2. Coloration rate η as a function of the light exposure wavelength for a bare WO_3 film (open symbols) and a CdS-WO_3 bilayer (closed symbols).

increase at higher energies (dotted line) E_G can be determined from the abscissa intersect. We found a value of about 2.54 eV which is somewhat higher than the band-gap energy of CdS single crystals (2.42 eV). This finding is in good agreement with the results of other authors using CBD prepared CdS films, and is usually ascribed to quantum size effects.^{13,14} According to Nedeljkovic *et al.*¹⁵ the shift of E_G corresponds to a mean-crystallite diameter of 7 nm. After the preparation of the CdS layers they were covered with a 200 nm thick tungsten oxide film which was thermally evaporated at a pressure of 10^{-5} mbar from WO_3 pellets. The WO_3 films thus prepared were amorphous as probed by x-ray measurements.

The CdS-WO_3 bilayers were illuminated with light from a 150 W xenon high pressure lamp which had passed a monochromator, in order to study the spectral sensitivity of the device. The light intensities the samples were exposed to were determined with a power meter and were on the order of several mW/cm^2 . The optical absorption was probed by the transmissivity of an incoherent light beam at a wavelength of 668 nm. When CdS films not covered with tungsten oxide were irradiated with wavelengths between 600 and 400 nm no change of the transmissivity of the probe beam was detected. By contrast, distinct temporal changes in the absorptivity were observed for the CdS-WO_3 bilayer as described in the following. We assign this effect to the coloration, i.e., photochromism, of WO_3 .

Since for short illumination times the coloration is found to increase linearly with time t , the slope of the obtained curves can be used to determine the coloration rate $\Delta\alpha/\Delta t$. The closed squares in Fig. 2 show the coloration rate η which has been normalized to the incident light intensity as a function of the incident wavelength λ for the CdS-WO_3 bilayer. For wavelengths above 525 nm, no photochromic effect could be detected; however, there is a strong increase of the coloration rate towards shorter wavelengths, whose onset roughly corresponds to the band-gap energy of CdS determined from Fig. 1. We will discuss this point in detail below.

The corresponding data for a bare tungsten oxide film are also plotted in Fig. 2 (open squares). As already mentioned, photochromism sets in only for wavelengths $\lambda < 380$ nm, i.e., in the ultraviolet range.⁶ Obviously the spectral sen-

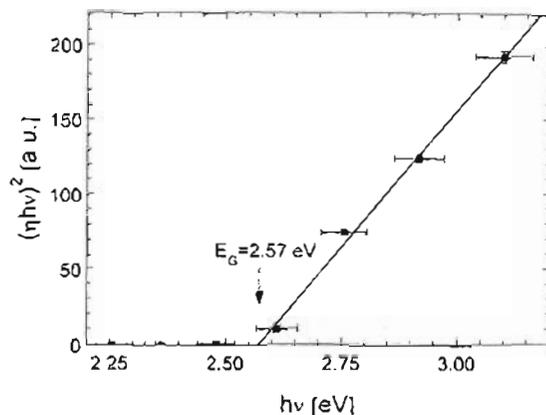


FIG. 3. Dependence of $(\eta h\nu)^2$ of a CdS-WO_3 bilayer on the light exposure energy. The similarity of this graph with Fig. 1 suggests a direct proportionality between η and α .

sitivity of photochromism of tungsten oxide in a CdS-WO_3 bilayer is shifted by more than 150 nm, compared to a bare tungsten oxide layer, well into the visible range. The maximum change of the absorptivity of the bilayer when exposed to a wavelength of 450 nm was determined to be on the order of 10%. This value roughly corresponds to what one finds for bare tungsten oxide thin films of comparable thickness after being exposed to ultraviolet light.

It has already been pointed out that the photochromic coloration of tungsten oxide is initiated by the optical excitation of electron-hole pairs. Consequently, one would expect the same spectral dependence of both the rate of coloration η and that of the electron-hole pair creation γ , the later being proportional to the absorption coefficient α . Near the band gap α to good approximation follows a relation:¹⁶

$$(\alpha h\nu)^{2n} \propto (h\nu - E_G), \quad (2)$$

where the exponent n depends on whether the transition is direct ($n=1$) or indirect ($n=4$). Indeed, in case of a single WO_3 thin film, where the above equation holds for $n=4$,¹⁷ the proportionality between η and α has already been demonstrated to be fulfilled.⁶

In the case of the CdS-WO_3 double layer, however, we assume the spectral sensitivity of photochromism in tungsten oxide to be dominated by the optical properties of the CdS layer. To study the relation between η and α in this case, we have plotted the coloration rate for the double layer taken from Fig. 2 according to the equation above with $n=1$ (see Fig. 3). Both the linear increase towards higher energies as well as the value for the band-gap energy obtained from a linear fit is very similar to Fig. 1 and thus shows that the coloration rate of the investigated tungsten oxide film is proportional to the absorption coefficient of the CdS layer underneath. This result is in good agreement with the current model for the photochromic effect of WO_3 where it is assumed that the formation of electron-hole pairs in tungsten oxide lead to a change of coloration. Apparently the CdS layer provides charge carriers to the adjacent photochromic material.

In order to understand the charge transfer processes in the vicinity of the WO_3 - CdS interface it is helpful to consider the band bending of such a heterojunction. Due to the

electron affinities and the positions of the Fermi levels we assume the conduction band of the CdS layer to be slightly above that of WO₃. Therefore, we favor the following model: After electrons and holes have been optically excited in the CdS layer, the former will be injected into the tungsten oxide due to the band bending. The holes decompose water molecules at the CdS-WO₃ interface via photoelectrolysis mentioned above [Eq. (1)] thus providing the other ingredient to WO₃ required for color center formation, namely protons. Accordingly, the CdS can be understood in terms of a photocatalyst for the photochromism of tungsten oxide. Indeed catalytic properties of CdS in CdS-WO₃ mixed semiconductors have already been observed by Ashokkumar *et al.*¹⁸ for the photoelectrolysis, i.e., the light-induced decomposition of water into hydrogen and oxygen which proceeds very similar to Eq. (1).

In summary we have shown that the sensitization to light exposure of tungsten oxide, i.e., photochromism, is shifted from the ultraviolet into the visible range if a thin CdS film is deposited underneath. The spectral behavior of the coloration rate turned out to be proportional to the optically excited electron-hole pair creation rate of the CdS thin film. The holes are believed to decompose water via photoelectrolysis on the CdS-WO₃ interface which is due to the high porosity of evaporated tungsten oxide present there to a considerable amount. Finally protons are formed which together lead with the optically created electrons to color centers in tungsten oxide. The results presented here might be of interest for certain applications like optical data storage devices. Furthermore, it increases our confidence in our model for the photochromic effect in WO₃.

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