Photoinduced doping of thin amorphous WO₃ films

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Abstract

During exposure of thin amorphous WO₃ films to UV light, both the optical absorptivity and the electrical conductivity increase. Using optically excited surface plasmons, we were able to measure even subtle changes of the absorptivity of 10 nm thick films simultaneously with their electrical resistivity at various temperatures. Our measurements show that the temperature dependence and the dependence on the density-of-states of the electrical conductivity in WO₃ can be explained by variable-range hopping of charge carriers between optically excited states near the Fermi level. Accordingly UV irradiation of tungsten oxide can be understood in terms of a photoinduced doping process which may have relevance for technical applications.

1. Introduction

Thin amorphous films of the semiconductor WO₃ are often discussed as active optical materials which are able to change reversibly their optical characteristics in the visible range in a controlled manner. This can be achieved, for example, by an electrochemical treatment or by UV light exposure of the sample, usually referred to as electrochromic and photochromic colouration respectively [1, 2]. It is evident that this behaviour offers a lot of promising applications such as flat panel displays [3] or active optical filters [4] which would overcome the deficiencies of the angle-dependent contrast of liquid crystals. Compared with the colouration behaviour much less attention has been paid so far to another feature which occurs simultaneously with increasing colouration of tungsten oxide, namely the increase of the electrical conductivity σ . It has been shown that the temperature dependence of films several hundred nanometres thick can be described in terms of a variable-range hopping (VRH) process [5, 6], which is often found to apply for amorphous semiconductors. There the current through the sample is ascribed to charge carriers moving between defect levels near the Fermi level E_F via a phonon-assisted tunnelling process. An estimate for the temperature dependence of this hopping conductivity in three dimensions has been given by Mott [7]:

$$\sigma[T, N(E_F)] = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^{1/4} \right] \quad (1)$$

where T is the temperature, $N(E_F)$ the density of states at the Fermi energy, $\sigma_0 \propto [N(E_F)]^{1/2}$ and $T_0 \propto 1/N(E_F)$. Up to now, however, the detailed nature of these defect

levels in tungsten oxide and their effect on the colouration was not clear.

The aim of this work is to investigate the relationship between colour centres and hopping states by the simultaneous measurement of the transverse electrical conductivity and the optical absorption of 10 nm thin amorphous tungsten oxide samples at different colouration levels in the temperature range between 300 and 200 K. In contrast to other authors, we were taking advantage of the photochromic effect, *i.e.* the UV-light-induced formation of colour centres, instead of the usually employed electrochromic colouration process. Although the latter method is more efficient in creating colour centres, the photochromic process avoids the poorly controlled conditions during the electrochromic colouration such as electrolytic side reactions or contamination of the sample with electrode material [8].

2. Experimental details

The change of the optical absorption α of the films was probed by means of optically excited surface plasmons propagating along a silver–WO₃ interface, using the so-called Kretschmann configuration. Here we shall describe this technique only briefly; for details we refer to ref. 9. Upon varying the angle of incidence of a p-polarized He–Ne laser ($\lambda = 633$ nm) a pronounced dip in the reflectivity R of the silver film is observed. Since the value of R in the reflectivity minimum depends strongly on the optical absorption of the tungsten oxide layer, this quantity can be used to resolve even minute changes in the optical absorptivity (although it does not yield absolute values of the

Fig. 1 Reflectivity R as a function of the angle of incidence Θ for a WO_3 film 10 nm thick before (—) and directly after (---) 5 min UV irradiation. The inset shows our sample geometry; hatched and dotted areas correspond to the Ag stripes and the subsequently evaporated tungsten oxide layer respectively.

absorbance) [9]. This is demonstrated in Fig. 1 where the reflectivity as a function of the angle of incidence Θ for a tungsten oxide film is plotted. The full and the broken curves correspond to an as-deposited and a UV-coloured sample respectively.

In order to measure the electrical conductivity of the tungsten oxide layer, the silver film was evaporated on the glass prism in three stripes separated by a gap of 0.5 mm, yielding two independent resistance bridges for the WO_3 sample. The sample geometry is shown in the inset of Fig. 1. The investigated tungsten oxide films were deposited at a pressure of 10^{-5} mbar from WO_3 pellets. During the evaporation process the substrate was at room temperature. The samples obtained in this way were amorphous as probed by X-ray measurements. Since both resistance bridges showed the same behaviour during our measurements, we conclude that the layers are quite uniform on the probed length scale.

Since the work function of the n-type semiconductor tungsten oxide has been determined to be 4.4 ± 0.1 eV which is considerably higher than that of thin evaporated silver films (3.5 eV [10]) we expect an ohmic rather than a Schottky contact between these layers. Accordingly we found a linear current-voltage characteristic. The applied voltage during the measurements was kept at $U = 10$ V.

Our measurements show that the transverse electrical current increases nearly linearly with increasing thickness of the tungsten oxide layer in the investigated range up to 400 nm. Therefore we conclude that the investigated 10 nm thick WO_3 layers already form a "homogeneous" film instead of isolated clusters on the substrate surface. Furthermore, this result shows that surface current effects are small compared with the bulk conductivity and can be neglected for our experiments.

The measurements were carried out in an optical cryostat. Creation of the colour centres was achieved by

irradiating the sample with the UV spectrum of an Xe lamp (350 mW cm^{-2}). In order to keep thermal effects to a minimum, wavelengths $\lambda \geq 450 \text{ nm}$ were suppressed with suitable optical filters. The sample was exposed to an oxygen atmosphere to force a complete bleaching of the tungsten oxide film after the irradiation [11]. In this way it was guaranteed that after each colouration-bleaching cycle the sample was in the initial state again. The conductivity measurements which are presented in this work were obtained at $T = \text{constant}$ as a function of the change of the colouration of the sample.

3. Results

Figure 2 shows the simultaneous measurement of the electrical conductivity σ and the change of the optical absorption α as a function of time t . The sample was exposed to UV light between $-20 \text{ s} \leq t \leq 0 \text{ s}$ which caused a strong increase of σ and α . At $t = 0$ where the irradiation was stopped a spontaneous decay starts which eventually leads to the initial state of the sample again. It is evident that the relaxation times of σ and α are quite different. After 100 s the value of the conductivity corresponds essentially to that before UV exposure whereas the absorptivity is still about one-half of the maximum value.

This different relaxation behaviour is also demonstrated in the inset of Fig. 2 where the conductivity as a function of the change of the absorption is plotted. Since we detected only changes of the optical absorption the origin of the abscissa was set to the value of the bleached state of the tungsten oxide film. (In the following it will turn out that our freshly evaporated films

Fig. 2. Temporal behaviour of the electrical conductivity and optical absorption during a colour-bleaching experiment at 300 K. The increase of the signals is due to the exposure of the tungsten oxide sample to UV light, whereas the decrease beyond $t = 0 \text{ s}$ corresponds to spontaneous relaxation. The inset shows the same data in a σ vs. α plot.

Fig. 3. Electrical conductivity of a WO₃ film 10 nm thick as a function of its optical absorption (at 633 nm) for various temperatures: ○, 300 K; ●, 280 K; □, 260 K; △, 240 K; ▽, 220 K; ■, 200 K; —, fits as discussed in the text.

have an initial absorptivity corresponding to $\alpha \approx 0.2$ in the units of Fig. 2).

We performed these measurements at various temperatures between 200 and 300 K. The resulting curves, plotted in Fig. 3, all show a roughly similar behaviour. For weakly coloured WO₃ films, σ is nearly constant, whereas upon further colouration a strong increase of σ is observed. Evidently, the onset of this increase shifts to higher absorption with decreasing temperature.

In the following we will analyse the data in terms of VRH, assuming that the randomly distributed colour centres which are responsible for colouration provide the defect states necessary for the electrical conductivity. Furthermore we assume at first a three-dimensional hopping process (see eqn. (1)), which means that the sample provides no geometrical constraints for the electrical conductivity, although the investigated samples are much thinner than those in refs. 5 and 6. This point will be discussed in detail below.

Accordingly, we can replace the density of hopping states $N(E_F)$ in eqn. (1) by the change of the absorptivity α . We then have to introduce an additional parameter α_0 , which takes into consideration that virgin WO₃ films already contain some stable colour centres which are usually generated during the evaporation process. Since the absolute value depends strongly on the preparation conditions [12, 13], α_0 corresponds to a free fit parameter. Thus the following expression is used to fit the data:

$$\sigma(\alpha, T = \text{constant}) = A(\alpha + \alpha_0)^{1/2} \times \exp\left\{-\left[\frac{B}{T(\alpha + \alpha_0)}\right]^{1/4}\right\} \quad (2)$$

where A , B and α_0 are free parameters adjusted by a least-mean-squares fitting routine. As Fig. 3 shows, our data are represented by this fit very well, for all temperatures investigated. From the fit parameters A , B and α_0

Fig. 4. Conductivity (on a logarithmic scale) plotted vs. $T^{-1/4}$ for amorphous tungsten oxide at three different absorptivities: ○, $\alpha = 0.4$; □, $\alpha = 0.35$; ▽, $\alpha = 0.3$. The curves are obtained from the data in Fig. 3 taking profiles parallel to the ordinate.

the values of T_0 and σ_0 can be determined using

$$T_0 = \frac{B}{\alpha + \alpha_0} \quad (3)$$

$$\sigma_0 = A(\alpha + \alpha_0)^{1/2} \quad (4)$$

When the parameters were adjusted separately for every temperature, the resulting values for T_0 and σ_0 varied by only 10%, thus increasing our confidence in their significance. For bleached films, *i.e.* $\alpha = 0$, we obtained T_0 and σ_0 to be 1.5×10^9 K and $2.7 \times 10^8 \Omega^{-1} \text{cm}^{-1}$ respectively, which is in accordance with the results of other authors [5, 6]. Furthermore these are reasonable values for VRH and in a range found for other amorphous semiconductors too [4].

An alternative representation of our data is given in Fig. 4, which shows the temperature dependence of the electrical conductivity $\sigma(T, \alpha = \text{constant})$ for three different absorptivity states ($\alpha = 0.3, 0.35$ and 0.4). The data points in a σ vs. $T^{-1/4}$ plot follow straight lines as expected for VRH.

4. Discussion

So far, the results indicate phenomenologically that colour centres in tungsten oxide are closely related to intermediate trapping states for electrons, forming a path for the conductivity. To explain the origin of this relationship from a microscopic point of view we have to discuss the physical nature of the colour centres.

Usually the optical absorption is attributed to the existence of a hydrogen–tungsten bronze HWO₃. The electrons are localized predominantly on tungsten atoms forming W^{+V} ions (W^{+V} denotes the valency

state + V), whereas the charge-compensating protons occupy adjacent interstitial sites between corner-sharing WO₆ octahedra [12, 15].

To contribute to the electrical conductivity there must exist additionally some unoccupied states for these localized electrons. Accordingly it has already been proposed by Crandall and Faughnan that the observed conduction characteristics can be explained by electrons hopping from W^{IV} to empty W^{VI} states adjacent to the protons which are assumed to remain fixed on their positions [5].

Consequently, deviations from local charge compensation are to be expected (global charge compensation is not affected since the total number of charge carriers is constant). At first glance, this seems unlikely to occur because of the strong Coulomb repulsion between the electrons. However, in the case of disordered transition metal oxides (such as WO₃), charges are likely to be effectively screened by the formation of small polarons which in the case of tungsten oxide give rise to an additional stabilization energy of 0.275 eV [16, 17]. Owing to the large static real part of the dielectric function in tungsten oxide ($\epsilon' \approx 20$ [1]) the Coulomb interaction between W^{IV} ions near the same proton will be small compared with the small-polaron binding energy.

When the single W^{IV} ions and adjacent protons are far away from one another the overlap of the wavefunctions between hopping sites is very small. With further colouration, however, the distance between W^{IV} sites decreases gradually, forming a path for the current by phonon-assisted tunnelling of electrons which leads to the observed strong increase of σ in Fig. 3.

From the above we will expect the number of hopping states to be of the same order of magnitude as the number of colour centres. Therefore, in the following, we want to estimate the density of hopping states $N(E_F)$ which can be obtained from T_0 using [18]

$$N(E_F) = \frac{21.2\xi^3}{kT_0} \quad (5)$$

where ξ represents the inverse decay length of the wavefunction of an electron at a hopping site. Using eqn. (3), we can write

$$N(E_F) = \frac{21.2\xi^3}{kB}(\alpha + \alpha_0) \quad (6)$$

which demonstrates that by changing the absorptivity α (colouration) we can continuously vary the electron density of states at the Fermi surface. This capability of *in situ* doping might be highly relevant for the development of sensor devices using WO₃.

Usually the value of ξ is estimated from [7]

$$\hbar\xi = (2mE)^{1/2} \quad (7)$$

Fig. 5. Comparison between the density of hopping sites, the absorptivity of the samples and the density of colour centres respectively: ○, the bleached state at various temperatures; ●, different absorptivity states (see Fig. 4).

where m is the electron mass and E is the potential depth of the hopping sites. To determine the latter quantity we refer to electrical conductivity measurements by Deb [1], who observed an exponential temperature dependence in tungsten oxide above room temperature, which is expected when electrons move across the sample by thermally activated jumps instead of phonon-assisted tunnelling. From the slope of an Arrhenius plot the average energy barrier between different sites had been determined to be $E = 1.04$ eV [1]. In case of an electron with the free electron mass we obtain $\xi^{-1} = 1.78$ Å which is a reasonable decay length and which is close to theoretical results for other amorphous transition metal oxides [7, 19]. According to eqn. (5) the density of hopping states $N(E_F)$ can now be calculated from T_0 as a function of the total optical absorptivity $\alpha_0 + \alpha$ of the sample. Taking into account that the width of the electronic levels created upon colouration is about 1 eV [20], the spatial density of hopping sites $n(E_F)$ can be determined. We obtain $3.3 \times 10^{19} \text{ cm}^{-3}$ and $8.7 \times 10^{19} \text{ cm}^{-3}$ for the bleached and the most strongly coloured state of our sample respectively. The results are plotted in Fig. 5, where the open symbols correspond to the bleached state ($\alpha = 0$) of tungsten oxide at various temperatures whereas the filled symbols mark the corresponding values obtained for the different absorptivity states in Fig. 4. The finite density of hopping states for bleached samples in this plot which has been ascribed to native colour centres is about $3 \times 10^{19} \text{ cm}^{-3}$.

As already mentioned, a change in eqn. (1) would be expected if the path of a charge carrier through the sample is restricted by the sample thickness d . According to Shante, the electrical conduction will then change from a three- to an essentially two-dimensional

behaviour [21]. This transition is only to be expected in very thin films where

$$d < \frac{1}{2\xi} \left(\frac{T_0}{T} \right)^{1/4} \quad (8)$$

In the two-dimensional regime Shante predicted that the exponent 1/4 in eqn. (1) changes to 1/3 and furthermore that T_0 is inversely proportional to the film thickness. In our case, however, the above criterion for two-dimensional hopping does not hold nor do we find a deviation from our T_0 values from that of other authors using considerably thicker films. This means that eqn. (1) has been correctly applied to our data.

Finally we compare the spatial density of hopping sites directly with the absolute density of colour centres instead of the absorptivity parameter α . This has been achieved by comparison of the absorptivities in Fig. 2 with the saturation value of the our sample. Since the saturation density of colour centres of photochromically coloured samples is well known [1, 22] we were able to rescale the absorption axis in Fig. 5 with respect to this quantity. The slope of the broken line which has been fitted to the data has a value of 2.1, which means that one colour centre in tungsten oxide provides approximately two hopping sites. This is consistent with the above idea, where we assumed that more than one electron can be localized near the same proton.

5. Conclusions

In summary we have shown that the electrical conductivity and the optical absorption of amorphous tungsten oxide films can be increased by UV exposure. The absorption dependence as well as the temperature dependence of the electrical conductivity turned out to obey Mott's VRH law often fulfilled for amorphous semiconductors. The linear relationship between the absorption of the sample and the density of states responsible for electron transport strongly suggested that the colour centres are closely related to trapping sites of electrons. This finding has been interpreted as small-polaron formation of conducting electrons at tungsten sites near to colour centres.

The results presented here might be of interest for certain applications. In contrast to other materials, where the density of states usually can only be influenced during the sample preparation process, the photochromic effect of tungsten oxide allows $N(E_F)$ to be adjusted *in situ*. If the WO₃ sample is stored in a non-oxidizing atmosphere, the density of states remains nearly unchanged, but will become zero upon oxygen exposure. As a consequence of the increase of $N(E_F)$ we

would expect simultaneously a shift of the Fermi level to higher values in the coloured state of the sample. This has been observed indeed in the case of electrochemically coloured tungsten oxide [20]. The *in situ* doping of WO₃ might have relevance to devices such as diodes with tunable current-voltage characteristics or temperature sensors with an adjustable operating range.

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