the other hand, owing to their stability, these membranes could find applications in particular processes in which organic membranes cannot be employed because of their higher degradability. Particularly promising could be their employment in fuel cells at high temperatures or in the concentration of wastes containing fission products.

Some acid salts with as yet unknown crystalline structures possess interesting ion-sieve properties; e.g., thorium arsenate behaves as a very narrow ion sieve and only H–Li exchange is therefore possible. This interesting property has already been employed for the separation of Li$^+$ from other cations.[64]

The very high selectivity of fibrous cerium phosphate for Pb^{2+} and certain other divalent cations is also very promising for practical applications.[44] Finally, impregnated papers or thin layers of insoluble acid salts have been successfully employed for several chromatographic separations of inorganic cations.[9,11,53,80]

Future Developments

In recent years much progress in both fundamental and practical aspects of layered exchangers has been made; however, further investigations, especially on the reticular position of counterions and solvent, on the variation of the selectivity with interlayer distance are still needed in order to understand in detail their ion-exchange mechanism and to make some predictions about their ion-exchange properties.

Concerning fibrous as well as needle shaped acid salts the preparation of crystals large enough for structural determination is the first important step for future progress.

An understanding of the reasons for which a given crystalline structure is formed is of utmost importance, and studies in this field will be also very useful for the synthesis of new inorganic ion-exchange materials.

Finally, studies on the surface properties, on the catalytic activity, and on the diffusion and electrical transport of counterions could lead to some important new practical applications of these materials.

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Photochromism and Electrochromism in Amorphous Transition Metal Oxide Films

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Much attention has recently been given to the phenomena of photochromism and electrochromism since their proposed application[1-3] in information display devices. The phenomena basically consist of the ability of certain materials to change their light absorbing properties when optically excited (photochromism) or while under the influence of an externally applied electric field (electrochromism). The induced coloration remains even after the excitation source has been removed. Technological interests result because the material returns to its original state upon either irradiation with light of the frequency corresponding to the induced absorption or by reversing the polarity of the externally applied electric field. Thus, the material behaves in a reversible manner, and it can be cycled at will. These phenomena, as first demonstrated by Pohl[4] with alkali halides, led to the present day concepts of color centers.[5] Current concepts of

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photochromism[6-8] and electrochromism[9] draw heavily from the many theoretical and experimental works on color centers.

The photochromic or electrochromic coloration of materials involves the trapping of electrons at appropriate lattice sites within the material which promotes the absorption of visible light. In the *electrochromic effect*, electrons are injected into these sites from an *externally applied electric field*, whereas in the *photochromic effect*, electrons are supplied to these sites by optical *excitation of electrons residing in the material*. This Account describes recent work[9-22] on some physical and chemical properties of amorphous transition metal oxide films that exhibit these effects. Particular emphasis is placed on the results obtained by x-ray photoelectron spectroscopy (XPS or ESCA) on both UV and electrolytically colored films. The present state of understanding of the photo- and electrochromic phenomena is reviewed and interpretative models are discussed.

Preparation of the Amorphous Films

Films of WO_3, MoO_3, and V_2O_5 are prepared by vacuum evaporation from electrically heated boats of W, Ta, or Mo. The oxides are deposited onto conducting glass substrates, known as NESA glass,[23] which have a chemically deposited coating of SnO_2. In our particular evaporation system, the base pressure of the chamber was in the upper 10^{-7} Torr range and rose to $\sim 5 \times 10^{-5}$ Torr during evaporation. Boat temperatures during deposition, as determined by an optical pyrometer, were typically ~1300 °C for WO_3, ~700 °C for MoO_3, and ~500 °C for V_2O_5. A quartz crystal oscillator was used to measure film thicknesses. These were 3000–6000 Å attained at deposition rates of 10 to 25 Å/s and a boat-to-substrate distance of 25 cm.

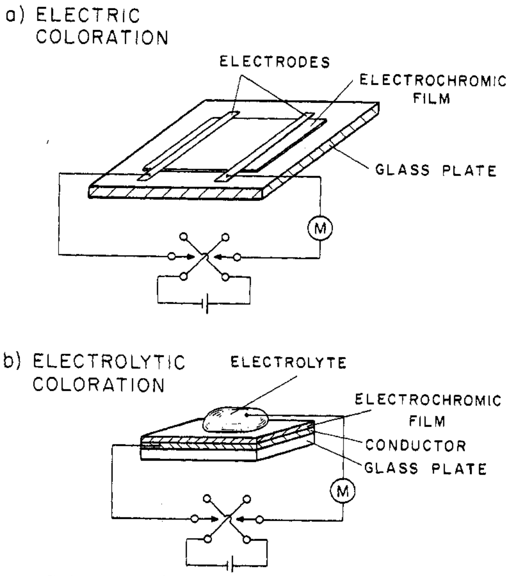

Figure 1. Schematic diagrams of electrochromic cells used for (a) electric coloration and (b) electrolytic coloration. Reproduced with permission from ref 11b. Copyright 1977 American Institute of Physics.

Freshly evaporated films of WO_3 and MoO_3 are transparent and V_2O_5 films are pale yellow. The films appear uniform under an optical microscope at a magnification of 100×, and x-ray and electron diffraction show that they are amorphous.

It is well known that some transition metal oxides exist in well-defined oxygen-deficient phases sometimes referred to as Magneli phases.[24,25] Such nonstoichiometric phases contain a large number of oxygen ion vacancies which can be formed by evaporation under the above conditions of vacuum and temperature. It has also been found[26,27] that some of these oxides evaporate congruently to form substoichiometric compositions, e.g., $WO_{2.96}$. Deb[16] estimated the density for amorphous WO_3 films to be 6.5 g/cm^3 as compared to a density of 7.3 g/cm^3 for crystalline WO_3. If the difference in densities is assumed to be associated with oxygen deficiencies in the amorphous film, then by direct proportion the O/W ratio in the amorphous film is 2.7. Hollinger et al.[13] in a recent XPS study of amorphous WO_3 films also determined an O/W ratio of 2.7 by using a proton backscattering technique. Likewise, Schirmer et al.[22] used x-ray fluorescence to observe a change in the oxygen content of WO_3 films upon annealing in air and an N_2 atmosphere. They observed an O/W ratio of 2.75 for air treatment and 2.60 for N_2 annealing. Berak and Sienko[28] have developed a chemical analysis technique to accurately determine the stoichiometry of a number of WO_{3-x} compounds.

Coloration of the Films

The films can be colored to a deep blue by three methods: (a) optical irradiation, (b) electrically, and (c) electrolytically. In the optical coloration method, the films are irradiated with light ($h\nu > 3.4$ eV) for several hours. Blue color develops gradually and grows more intense with prolonged exposure. This phe-

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nomenon is photon-induced coloration and is called photochromism.

In the latter two methods the color is induced by an electric field, a phenomenon known as electrochromism. Considering the second method, electric coloration, we refer to the surface electrode configuration of Figure 1a. These electrodes can be either vacuum-deposited gold or hand-painted conductive films. Application of a dc electric field of $\sim 10^4$ V/cm between the electrodes causes a blue color to appear at the cathode side (–) which then propagates toward the anode. Coloration is slow; several hours are required to color the entire interelectrode region. On reversing the polarity, the blue color migrates back toward the newly formed anode and disappears into it; then fresh coloration begins at the new cathode. Once a film is colored, it retains its color after the voltage is removed for an indefinite period.

A preferable arrangement is a sandwich structure in which a film is placed between a pair of transparent electrodes. Electrodes are normally composed of either SnO_2 or In_2O_3 which has been chemically deposited. A typical sandwich configuration would be glass/SnO_2/MO_3/SnO_2. Application of an external potential (1 to 3 V dc) between the conducting electrodes is sufficient to maintain a strong electric field capable of forming a large density of color centers in a short period of time, i.e., a few seconds. However, on reversing the polarity, no bleaching can be observed. This is due to the newly formed cathode attempting to inject electrons into the electrochromic film. This lack of reversibility limits its practical application.

It is possible to achieve reversibility by deliberately making the cell asymmetric, e.g., introducing an insulating layer between one of the oxide–electrode interfaces. A typical configuration might be glass/SnO_2/MO_3/SiO_2/SnO_2. When a dc voltage is applied across such a cell so that the electrode adjacent to the electrochromic film is made negative, electron injection into the film occurs and the oxide layer colors deep blue. On reversing the polarity, electron injection from the newly formed cathode is prevented by the insulating layer. The trapped electrons can then empty into the newly formed anode resulting in bleaching of the film.

The third method, reversible electrolytic coloration, is to separate the top oxide–electrode interface by a pool of electrolyte,[17-19] e.g., an acid electrolyte with a Pt wire electrode dipped into it serves the purpose (Figure 1b). Using the electrode adjacent to the film as the cathode and the Pt wire as the anode, the film colors rapidly. On reversing the polarity, electrons released by the newly formed cathode (the Pt wire) can combine with protons in the electrolyte forming H atoms and subsequently H_2 gas; this allows the trapped electrons in the film to escape to the anode. The film again bleaches. This rapid process of coloration/bleaching can be repeated many times. WO_3 and MoO_3 films are colored with the aid of an acid electrolyte consisting of H_2SO_4 in water and glycerol. V_2O_5 films are colored with an electrolyte of LiCl in absolute methanol since V_2O_5 films dissolve in acid and/or aqueous solutions.

Characteristics of the Films

Details of the physical properties of the UV and electrically colored films have been reported by Deb.[14-16] Listed below is a summary of the experimental observations made by Deb and/or ourselves on these films.

(1) Coloration occurs most efficiently when the films are highly disordered (amorphous). Fully oxidized crystalline films do not show any coloration except for those formed at high temperatures under a reducing atmosphere (e.g., heating in vacuum or in a hydrogen atmosphere).

(2) The color centers are normally stable and do not show any bleaching when irradiated with light of frequency corresponding to the induced absorption.

(3) Bleaching of the color centers can be achieved by heating in an oxidizing atmosphere at a temperature near 300 °C. Once the film is oxidized, however, it does not lend itself to further coloration.

(4) Heating freshly evaporated thin films in the presence of oxygen at 300 °C initially produces color centers, but eventually bleaches them.

(5) Heating under the conditions of (4) but in an argon atmosphere produces the same coloration without bleaching.

(6) Freshly evaporated films of MoO_3 give an electron spin resonance (ESR) signal characteristic of Mo^{5+} (i.e., $g = 1.924$) which increases slightly with coloration. Bleaching the film in oxygen at 300 °C causes the ESR signal to disappear completely.

(7) The coloration is associated with a great increase in dark conductivity of the material. Upon irradiation with light of frequency within the induced absorption band, photoconductivity can be observed only at high electric fields and elevated temperatures.

(8) Enhanced absorption in the visible and near-infrared spectral regions is observed for colored films of WO_3 and MoO_3 except for a small window in the blue region. Spectra of optically and electrically colored films are similar.

(9) Coloration efficiency increases with increasing temperature up to a maximum of $\sim$80 °C, above which it decreases again.

(10) Optical and electrical colorations are sensitive to ambient conditions, i.e., coloration efficiency increases in the presence of moisture and no electric coloration was observed in high vacuum, although optical and thermal colorations still occur.

Faughnan et al.[9] have recently added several new observations for electrolytically colored films:

(1) The charge removed during the bleaching pulse is equal to the charge injected by the coloring pulse.

(2) The color center concentration ranges between 10^{19} and 10^{22} cm^{-3} for optically and electrolytically colored films, respectively.

(3) The negative charge carriers in the films are electrons.

(4) The magnitude of charge injection during coloration suggests a double injection process in which positive charge compensating ions are introduced. Protons are the charge compensating ions when acid electrolytes are employed.

(5) A large density of hydrogen in the WO_3 lattice results in the formation of hydrogen tungsten bronzes, H_xWO_3.

Photoelectron Spectra

Rabalais, Colton, and Guzman[10] were first to observe the change in the valence band structure between transparent and electrolytically colored films of MoO_3.

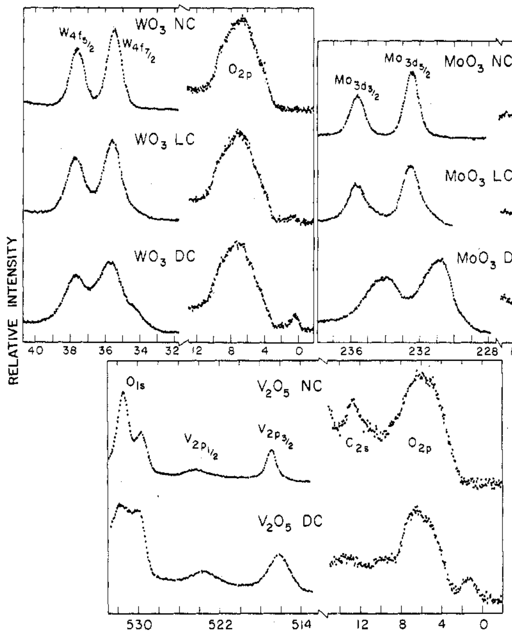

Figure 2. Photoelectron core level and valence band spectra of WO_3, MoO_3, and V_2O_5 films. NC = not colored; LC = lightly colored; DC = deeply colored. Reproduced with permission from ref 11b. Copyright 1977 American Institute of Physics.

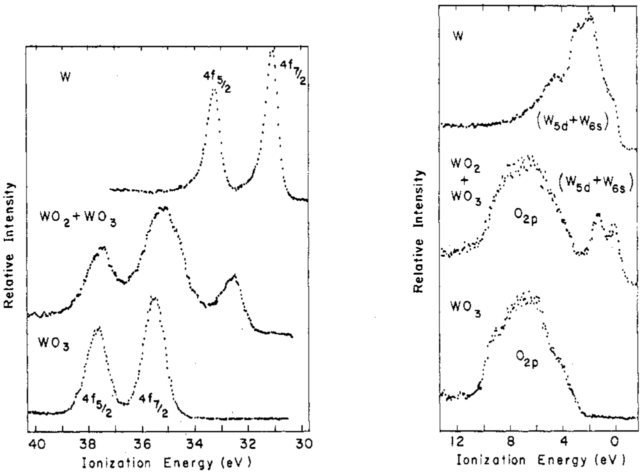

Figure 3. Photoelectron core level and valence band spectra of W and its oxides.

Table I

Photoelectron Ionization Energies (in eV)[a] from Some Core Levels of W, Mo, V, and Their Oxides

Sample[b]	$W\ 4f_{7/2}$	$W\ 4f_{5/2}$	O 1s
W (G)	31.2 (1)	33.4 (1)	-
WO_2[c]	32.5 (1)	-	530.2 (1)
WO_3	35.5 (1)	37.6 (1)	530.3 (1)
$H_{0.5}WO_3$	35.6 (1)	37.7 (1)	530.3 (3)
H_2WO_4	35.1 (2)	37.3 (2)	530.0 (2) 532.5 (2)
WO_3 (NC)	35.5 (1)	37.7 (1)	530.6 (1)
Sample[b]	$Mo\ 3d_{5/2}$	$Mo\ 3d_{3/2}$	O 1s
Mo (G)	227.8 (1)	231.0 (1)	-
MoO_2 (S)	229.1 (1)	232.3 (1)	530.4 (1)
MoO_2 (NS)	229.1 (1)	233.4 (1)	530.0 (1)
MoO_3	232.5 (1)	235.7 (1)	530.3 (2)
MoO_3 (NC)	232.5 (1)	235.5 (1)	530.3 (1)
Sample[b]	$V\ 2p_{3/2}$	$V\ 2p_{1/2}$	O 1s
V (G)	512.1 (1)	519.7 (2)	-
V_2O_3 (S)	515.5 (1)	523.0 (1)	530.3 (1)
V_2O_4 (S)	516.1 (1)	523.3 (1)	530.2 (2)
V_2O_5	517.0 (1)	524.4 (1)	529.8 (1)
V_2O_5 (NC)	516.9	524.3	529.9 531.6 (glass)
V_2O_5 (DC)	516.2	523.5	530.3 531.5 (glass)

[a] Numbers in parentheses represent uncertainties in the number(s) to the right of the decimal. [b] G = mechanically ground in vacuum; S = sputtered with 500-V Ar^+ ions; NC = not colored (evaporated film before electrolytic coloration); DC = deeply colored electrolytically; NS = not sputtered. [c] Partially oxidized to WO_3.

A recent study[11] of WO_3, MoO_3, and V_2O_5 films which were colored electrolytically by both acid and alkali metal electrolytes has been published. This study reveals gross changes in both valence and core level XPS spectra. Hersch, Kramer, and McGee[12] have recently reported similar XPS results on WO_3 and Hollinger, Duc, and Deneuville[13] have investigated in situ UV-colored films of WO_3. These XPS results are reasonably consistent.

Examples[11] of the XPS spectra of the valence bands and W 4f, Mo 3d, V 2p, and O 1s bands of electrolytically colored films of WO_3, MoO_3, and V_2O_5 are shown in Figure 2. The principal valence band structure results from the photoejection of O 2p electrons. The major difference in the valence bands is near the Fermi level where the colored films exhibit a small band. The intensity of this band is proportional to the degree of coloration of the film. There is an indication of this band in the uncolored film which appeared only after several hours of x-ray irradiation; this film developed a faint blue color in the region of irradiation. The core level spectra resulting from photoejection of W 4f, Mo 3d, and V 2p electrons show the line shape of the two spin–orbit split components becoming asymmetric with coloration.

The appearance of the small band near the Fermi level and the asymmetry of the core levels upon coloration are interpreted as follows. Consider the case of WO_3. If WO_3 is completely ionic, i.e., W^{6+} and O^{2-}, the valence band would consist of oxygen 2p states and the conduction band would be composed of empty tungsten 5d and 6s states. The addition of electrons would result in the occupation of some of these empty 5d and 6s states. This occupation can be illustrated for tungsten in 0, +4, and +6 "formal oxidation states" by reference to the PE valence band spectra of W, WO_2, and WO_3 in Figure 3. These spectra indicate that the W 5d and 6s states are occupied (containing six electrons) in W metal, partially occupied (containing two electrons) in WO_2, and empty in WO_3. Shifts in the core levels also result from changes in chemical environment; this change is known in XPS as the chemical shift. Chemical shifts in the W 4f core levels of W, WO_2, and WO_3 are also illustrated in Figure 3. Here the magnitudes of the shifts are large enough to allow unambiguous identification of the chemical states present. The center plot shows the presence of WO_3 in addition to WO_2. It can be seen from Table I and the above spectra that the WO_3 NC (not colored) film most closely resembles WO_3. However, upon coloration, the presence of the additional band in the valence region and the asymmetry in the line shape of the core levels suggest that some of the tungsten is being reduced to a state of lower oxidation. In fact, we estimate this state to be somewhere between W^{6+} and W^{4+}. Deconvolution of similar bands into W^{6+} and W^{5+} levels with their corresponding plasmon satellites has been presented by Hollinger et al.[13] The shift of the 4f levels between W^{6+} and W^{5+} is ~1.2 eV.

The PE spectra of the substoichiometric MoO_3 and V_2O_5 films and Mo, V, and their oxides exhibit peaks which are very similar to those of the tungsten system. The interpretation of the tungsten system can be applied to these by using the appropriate metal valence bands. These are the 4d and 5s bands for molybdenum and the 3d and 4s bands for vanadium. The vanadium system is different from the tungsten and molybdenum systems in that V metal has five valence electrons and it has stable oxidation states of +3, +4, and +5. The uncolored V_2O_5 films have spectra similar to stoichiometric V_2O_5 and the colored films are similar to those of V_2O_4. Coloration has obviously reduced the V^{5+} to a lower oxidation state, possibly V^{4+}.

Model for Photochromism and Electrochromism

The spectroscopic results confirm: (a) that upon coloration reduced-state species are formed and upon bleaching they disappear again, (b) that appearance of the band near the Fermi level is associated with coloration and formation of the reduced-state species, (c) that this band is localized within the band gap of the original material, and (d) that the appearance of the asymmetric line shape of the metal core levels is also associated with the coloration and formation of the reduced-state species.

The currently adopted model[9,20,21] for electrolytic coloration of electrochromic films is that of a double injection process in which the negative charge carriers are electrons and hydrogen ions (from the acid electrolyte) are the charge compensators. The large density of protons which must occupy sites within the electrochromic material is believed to be in the form of a hydrogen metal bronze. (Bronzes[29,30] are well-defined nonstoichiometric compounds of the general formula $M_xT_yO_z$ where T is a transition metal such as W, Mo, V, Nb, or Ti as its highest binary oxide, T_yO_z, and M is some other metal or species such as H, Li, K, NH_4, Ag, etc. The variable x lies in the range $0 < x < 1$.) In order to confirm this, we measured[11] the PE spectrum (Table I) for commercially available $H_{0.5}WO_3$. The W 4f core levels show asymmetry in band shape similar to that found for WO_3 LC and the small band near the Fermi level is observed. In a recent PE study of some sodium tungsten bronzes,[31] the valence region showed a band near the Fermi level in addition to the O 2p band. Its area increased in proportion to the Na content. The band structure is believed[32-34] to be predominantly W 5d and filled by electrons donated by Na. Hollinger et al.[13] independently arrived at the same conclusion by measuring the α particles emitted from UV-colored WO_3 films by means of the nuclear reaction

$$^{11}B + H \rightarrow \alpha + {}^{8*}B \qquad (1)$$

They found x in $H_xWO_{2.7}$ to vary between $0.25 < x > 0.5$.

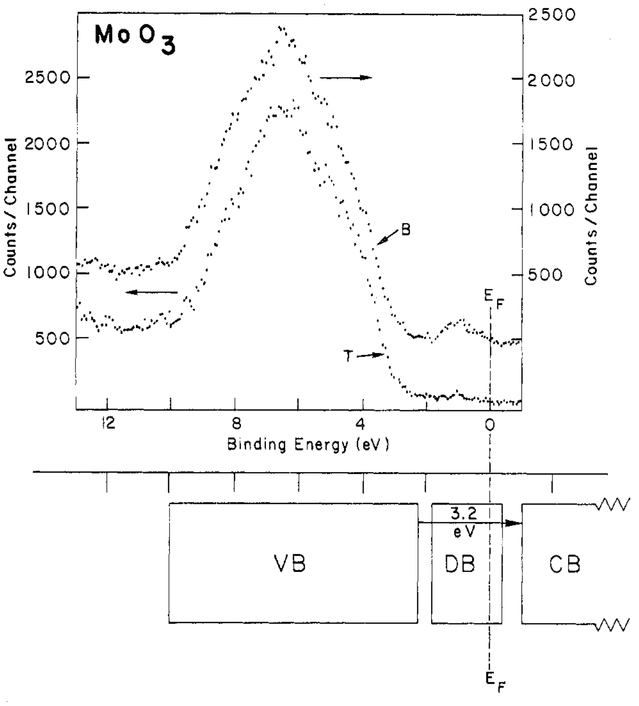

Figure 4. (Top) Photoelectron valence band spectra of T (transparent) and B (blue) MoO_3 films. (Bottom) Energy level diagram for MoO_3 near the Fermi level (E_F). Arrow indicates optical absorption edge. VB = valence band; CB = conduction band; DB = defect band.

It is difficult to prove that a hydrogen tungsten bronze is formed in the WO_3 films using XPS because the photoionization cross section of hydrogen is so small that it is not detected. Bronze formation,[29] however, is not unique to hydrogen, but it occurs with alkali and some transition metals. Colton et al.[11] investigated the possibility of bronze formation using ions other than hydrogen; electrolytes containing LiCl, NaCl, KCl, CsBr, and $MgCl_2$ salts were employed. If any of these ions become injected into the films, as hydrogen is believed to be, with sufficient concentration, they would be detected by a PE experiment. The experiments indicated that: (a) the films can be colored with various electrolytes; (b) alkali tungsten bronzes are being formed in the colored films; (c) the diffusion coefficients for these ions are most likely higher in the films than in single crystal bronzes. Green et al.[21] have also observed rapid diffusion of metal ions along grain boundaries of polycrystalline WO_3 films.

Most photochromic and electrochromic materials are either large band gap insulators or semiconductors and therefore should be transparent in the visible spectral region. Let us use MoO_3 as an example. The optical absorption spectrum of the MoO_3 NC film shows slight absorption in the visible and near-infrared. The fundamental absorption edges[33] give an estimate to the band gap; for MoO_3 NC it is ~3.2 eV. Coloration of the film results in the formation of a reduced state species whose origin is believed associated with the Mo 4d state. This species forms a defect band that is

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(29) For a review, see, for example, P. G. Dickens and M. S. Whittingham, *Q. Rev., Chem. Soc.*, **22**, 30 (1968), or *Adv. Chem. Ser.*, **No. 39** (1963).

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localized within the band gap (Figure 4). Optical absorption transitions from the valence band (O 2p in this case) to the defect band can result from photon irradiation. Population of the defect band in this way causes the formation of color centers. This is the phenomenon of photochromism. Thermal excitation of valence band electrons to the defect band may also result provided that the band gap is not too large. Once the defect band is populated, photon or thermal excitation may depopulate the band, causing the color centers to be bleached.

If an electric field is applied to the film in such a way as to sufficiently bend the bands, electrons from an external source can fill the defect band. This is the phenomenon of electrochromism. Higher electron population densities can be obtained in this way. The material also undergoes an insulator to semiconductor transition in which the band gap becomes smaller due to the repositioning of the Fermi level. Charge neutrality is obtained by simultaneous injection of ions from the electrolyte. Green et al.[21] have proposed the reaction: WO_3 (colorless) + $xM^+ + xe^- \rightleftarrows M_xWO_3$ (blue). Chang et al.[20] have suggested a different reaction: $mWO_3 + 2nH^+ + 2ne^- \rightleftarrows W_mO_{3m-n}$ (blue) + nH_2O. In light of the XPS data for WO_3 and MoO_3 films, bronze formation, as the first reaction, appears to be evident. For V_2O_5 films in which a complete reduction of V^{5+} to V^{4+} is observed, the second reaction might be more applicable. In either case, reversing the polarity of the applied electric field bends the bands in the opposite direction, allowing depopulation of the defect band; this causes the film to bleach.

The origin of this color center absorption is still a subject of debate, but is believed[9] to fall under one or more of the following categories where the absorption is due to (1) an intervalence transfer or small polaron absorption,[22] e.g., electron excitation between M^{5+} and M^{6+} ions, (2) charge transfer from the valence band of the material to an electronic state of a reduced species, e.g., a charge-transfer transition from the oxygen valence band (O 2p) to the M^{5+} state (W 5d) which is localized within the band gap, (3) interband transitions from filled bands to higher excited state bands, e.g., π^* to σ^* absorption as in ReO_3 compounds, and/or (4) F or F^+ centers in oxygen ion vacancies.[16]

We propose that vacuum deposition of these oxides produces an amorphous film that contains a large number of oxygen vacancies. When electrons are supplied from an external or internal source, they populate the defect band. The distribution of the extra electron is largely on the metal ions as indicated by the XPS results. The removal of oxygen decreases the Madelung potential at the metal site and thus the electronic state associated with the metal ion drops in energy from the conduction band into the band gap to form a localized state (Figure 4). For a WO_3 lattice, the metal site would be tungsten. Again assuming an ionic model for WO_3, i.e., W^{6+} and O^{2-}, the extra electron would occupy W 5d and 6s orbitals. This would effectively reduce one tungsten atom to a W^{5+} valence state. Charge compensation results when hydrogen ions supplied from an external source (either the acid electrolyte pool or moisture in the atmosphere) diffuse into the lattice. In vacuo coloration of films may rely on residual contaminates for compensating ions.

The WO_3 and MoO_3 data tend to support the intervalence or small polaron absorption model where the optical absorption results from transitions between M^{5+} and M^{6+} ions. For V_2O_5, in which the XPS data indicate a complete reduction of V^{5+} to V^{4+}, a charge-transfer model involving O 2p and V 3d states might be appropriate. Deb[16] observed that once the films become oxidized and crystalline, i.e., the oxygen vacancies are annihilated, no coloration occurred. It has recently been shown[22] that crystalline films can still be colored electrolytically and that the only difference is in the net absorbance and position of the absorption band. It appears that the degree of crystallinity plays an important role with regard to film stability and coloration efficiency and speed.

The nature of the band near the Fermi level in the PE spectra of colored films is due to the population of metal d or s bands (e.g., 5d or 6s of W, 4d or 5s of Mo, 3d or 4s of V). It is more likely the d bands due to the absence of a Knight shift in the nuclear magnetic resonance spectra of tungsten bronzes.[34] A Knight shift occurs for many metals; it is a large chemical shift in the NMR signal to lower magnetic fields relative to the signal for the same nucleus in some nonmetallic environment. Its magnitude is directly proportional to the electron density of the conduction electrons at the nucleus. Electrons in s orbitals or bands can contribute to the shift whereas those in p or d orbitals cannot.

Theoretical considerations[35] dealing with the photoionization cross section of trapped electrons indicate that electrons trapped by anion vacancies are likely to be observed by a PE experiment if they are associated with empty d orbitals of the surrounding metal ions, but they are unlikely to be observed if they are associated with empty s or p orbitals of the surrounding metal ions (e.g., alkali halides). A PE investigation of alkali halides doped with nonstoichiometric amounts of impurities has been conducted[36] in order to test this prediction. γ irradiation of these crystals produces high densities of color centers. PE data collected on some irradiated and nonirradiated crystals showed no detectable differences, in agreement with the theoretical predictions.

Conclusions

In conclusion, the XPS results for UV and electrolytically colored films showed that upon coloration (1) reduced-state species of some of the metal ions are formed, (2) population of empty metal d bands located near the Fermi level result, and (3) charge-compensating ions cause bronze formation. Bleaching the films causes a reversal of the processes.

Due to the almost instantaneous coloration/bleaching possibilities, the films have considerable application as digital display devices. Such devices would have several advantages over LED's (light-emitting diodes). They are inexpensive and compact, can be easily seen in bright sunlight, and can be made in different colors. Due to the disorder (amorphousness) that already exists in these materials, they can be designed for insensitivity to fast neutron bombardment and transient γ radiation resulting from a nuclear detonation; this might make amorphous devices attractive for military applications. A disadvantage is that they cannot be seen in dark

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conditions unless an external light is provided. In order to achieve efficiency and longevity for such applications, it will be necessary to obtain a more complete understanding of the electrochromic process. Further avenues for study are: (a) determining the ionic conductivity of hydrogen and other ions in these films, (b) using dopants to increase film stability and provide different colors, and (c) counting the number of electrons injected into the film during coloration and relating this to the density of electrons in the defect sites.

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