The semiconductivity and stability of palladium oxide

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Films of palladium oxide of good optical quality have been prepared by the oxidation of sputtered films of palladium. Optical absorption and photoconductivity measurements indicate extrapolated band gaps of 2.13 ± 0.03 eV and 2.67 ± 0.03 eV respectively with the photoconductivity showing an exponential tail extending to lower energies. Measurements of the thermal stability of the films in the presence of a low partial pressure of oxygen indicate a dissociation enthalpy of -1.17 ± 0.06 eV. The presence of hydrogen in the ambient during decomposition was found to reduce the temperature for decomposition to palladium metal from about 580 to 350 K.

1. Introduction

Semiconductors with a band gap that can couple efficiently to the solar spectrum are of interest for energy conversion applications either as photovoltaics [1], photocatalysts [2] or as electrodes for photoelectrolytic cells [3-9]. Palladium oxide is a useful catalyst and also a semiconductor with an estimated band gap near 820 nm, so an exploration of its properties for use in photoelectrolytic cells seemed justified.

Okamoto and Aso [10] have reported measurements of the electrical properties of thin films of PdO which indicated that it has a band gap of about 1.5 eV and behaves as a p-type semiconductor with a hole mobility of about $17 \, \text{cm}^2 \text{V}^{-1} \, \text{sec}^{-1}$. These authors also studied the stability of the oxide in a hydrogen ambient and indicated that the oxide was reduced at temperatures of the order of 300 K. Rogers et al. [11] grew crystals of PdO by vapour transport techniques and from the temperature dependence of their resistivity determined activation energies in the range between 0.04 and 0.1 eV which they attributed to a high density of acceptor levels that gave rise to extrinsic p-type conductivity. The nature of the charge carriers was determined from measurements of the Seebeck coefficients referred to copper as a standard. Bell

et al. [12] made measurements of the equilibrium dissociation pressure of PdO over the temperature range between 800 and 1150 K and found the expected exponential dependence of the equilibrium partial pressure upon temperature, characterized by an activation energy of -1.12 eV and in good agreement with previous measurements of Wöhler [13].

This paper reports optical and electrical conductivity measurements made on palladium oxide thin films to determine their band gap, conductivity and thermal stability in a vacuum and in the presence of hydrogen.

2. Experimental

Palladium metal films were prepared on quartz substrates by r.f. sputtering from a pure palladium target in an argon atmosphere. The film thicknesses were determined by weighing reference substrates before and after deposition using a microbalance with an accuracy of 10^{-6} g. Film thicknesses were varied between 480 and 2200 Å. These films were then oxidized in air or an oxygen atmosphere at a temperature of 700° C for periods between 24 h and 6 days. Either treatment produced good quality thin films of PdO with a uniform orange transmission. The stoichiometry

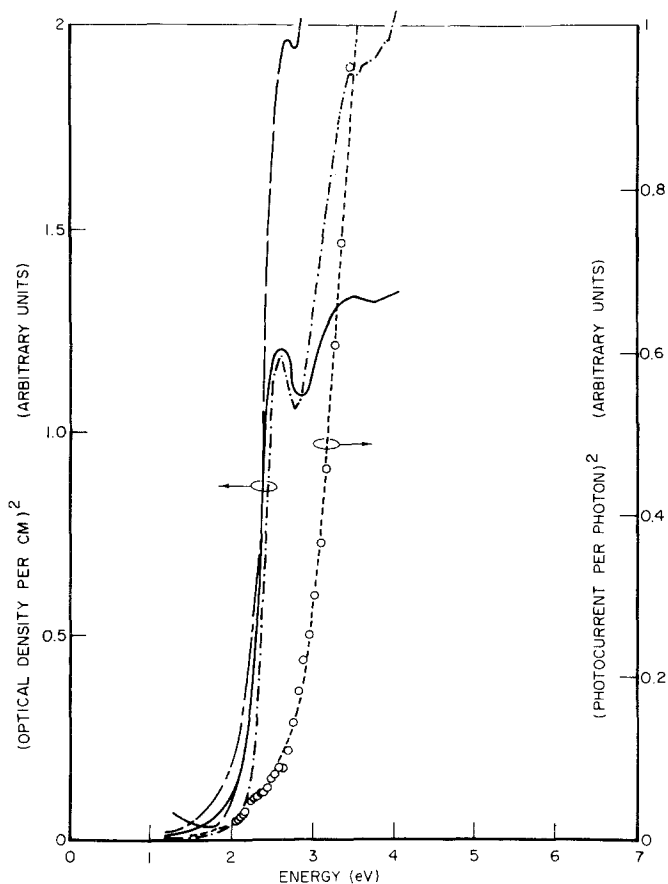*Permanent address: Department of Chemistry, University of Jordan, Amman, Jordan.

these films was estimated by determining the mass of the Pd film prior to oxidation and reweighing after the oxidation process. The experimental weight increase of the oxide over the sputtered palladium film of 13 ± 4% compares well to the expected percentage increase of 15% assuming the complete conversion of the palladium film to palladium oxide. Other possible oxidation products such as PdO · H_2O, PdO_2, PdO_2 · H_2O would give rise of weight increases of 32%, 30%, and 47%, respectively and in addition are extremely unstable forms of the oxide at the high oxidation temperatures used in these experiments. The optical absorption spectra of these thin PdO films was measured over the range between 200 nm and 40 μm. For the range between 2.5 and 40 μm a Beckman IR10 spectrophotometer was used in the double beam mode with an uncoated quartz substrate in the reference beam. This compensated for the (OH) absorption associated with the quartz substrate. No structure due to the PdO films was observable in this spectral range and, in particular, no absorption associated with (OH) could be detected.

The spectral range between 2 μm and 200 nm was examined using a Cary 14 spectrophotometer. The optical density of several films of different thickness was studied at both room temperature and at liquid nitrogen temperature. Typical room temperature data is shown in Fig. 1. Some sharpening of the observed structure occurred at liquid nitrogen temperatures but no shifts in the positions of the bands. The onset of strong optical absorption in the region between 1.7 and 2.5 eV and the absence of structure in the absorption spectrum at lower photon energies suggests that band to band transitions occur in this region. On the basis of this data an optical band gap of about 2.2. eV is indicated.

In an attempt to obtain an independent measure of the band gap, photoconductivity experiments were performed. These were complicated by the low sample resistivity which contributed a dark current some seven orders of magnitude larger than the photocurrent. Cooling the sample to liquid nitrogen temperature made only a small reduction in the dark conductivity. Lock-in techniques were therefore employed to measure

the photocurrent. This was done by chopping the light from the monochromator and measuring the a.c. sample current induced by the light with a P.A.R. model 121 lock-in amplifier synchronized to the chopping frequency. The light energy was varied using a Bausch and Lomb #33-86-76 high-intensity monochromator with a band pass of 13 nm coupled to a 150-watt xenon light source. The results, normalized to take into account the spectral dependence of the photon flux, are also plotted in Fig. 1. A least-squares fit of both the optical and photoconductivity data to an expression $K \propto (h\nu - E_{gap})^{1/2}$ (where K is an absorption constant) characteristic of direct gap photon transitions, yields an extrapolated optical band gap of 2.13 ± 0.03 eV and a photoconductive band gap of 2.67 ± 0.03 eV. Photoconductivity is detectable for values of energy smaller than the extrapolated band gap and shows an exponential shape characteristic of an Urbach tail.

In order to study the thermal decomposition of the PdO thin films their resistance was measured as a function of temperature using four collinear electrodes in contact with the film. A constant d.c. current from the regulated-current mode of a Kepco-ABC power supply was sent through the outer electrodes while the potential induced at the inner contacts was measured using a Keithley 160B digital multimeter. Reproducible spacing between the contacts was not possible with this configuration; thus no accurate values of resistivity were obtained (the average value, however, is approximately 0.04 Ω cm).

During these measurements the samples were contained in an ultra high vacuum system equipped with a U.T.I. Quadrupole mass spectrometer which was used to monitor the expected decomposition products as well as the partial pressure of trace gases in the system. Controlled partial pressures of various gases could be introduced into the system and the film stability studied in their presence. A helium–neon laser and photodetector was used to monitor the optical density of the film at 632.8 nm during these measurements. With the film in a vacuum ambient, several heating and cooling cycles between room temperature and 450 K established a repeatable state of the oxide characterized by a temperature coefficient of resistance of $-(3.6 \pm 0.4) \times 10^{-3}$ K^{-1}. The corresponding activation energy associated with the conductivity is $(2.6 \pm 0.3) \times 10^{-2}$ eV, which indicates that the
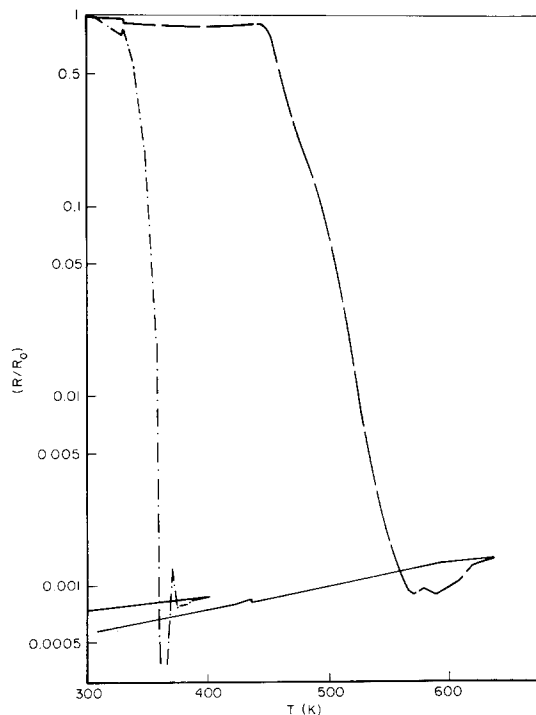

Figure 2 Normalized resistance as a function of temperature in K. Conditions: (— —) 5×10^{-8} torr vacuum, (—·—) 0.2 torr hydrogen. Upon cooling after decomposition, the temperature coefficients of resistance shown are (— —) 3×10^{-3} °C^{-1}, (—·—) 1.7×10^{-3} °C^{-1}.

conductivity is extrinsic and dominated by the presence of shallow trap levels.

If the samples were heated at a rate of 1 to 2 K min^{-1} beyond 500 K a sharp drop in the resistivity occurred and if heating was continued to 570 K or higher the films reverted to their initial metallic condition and oxygen evolution was detected with the mass spectrograph. After this decomposition the temperature coefficient of resistance of the metallic films was found to be $(3.3 \pm 0.6) \times 10^{-3}$ K^{-1}, which compares well with values for metallic palladium reported in the literature [14]. This behaviour is shown in Fig. 2.

If the decomposition was not taken to completion, but the sample cooled after being heated to some temperature below that required for complete decomposition, the material still exhibited semiconducting behaviour but with a lower resistivity and lower activation energy associated with the conductivity. Oxygen evolution associated with this pre-decomposition phase was not detectable with the mass spectrometer. A
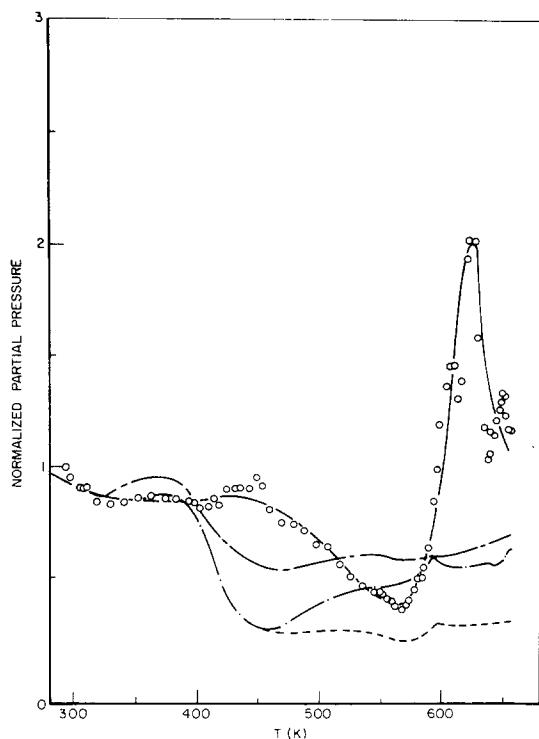
Figure 3 Normalized partial pressures of various gases as a function of temperature (in K) for the decomposition of PdO under high vacuum at a rate of $1.8^\circ C\,min^{-1}$. (—○—) O_2,(— — —)0, (— · —) He, (— — —) H_2.

Figure 4 Dissociation pressure of palladium oxide (in torr) as a function of reciprocal temperature (K^{-1}). ○ : Data of Bell, Inyard and Tagami $\Delta H_0 = -1.12 \pm 0.09$ eV; △ : Our data. This data, with the data of Bell *et al.* yields $\Delta H_0 = -1.17 \pm 0.06$ eV.

change in the optical density of the films did, however, occur.

Fig. 3 shows the partial pressures of various gas species as a function of the sample temperature during a decomposition experiment. Due to a change in the temperature of the vacuum chamber walls and the sample holder during the experiment, there is an increase in the partial pressures of all detectable gases in the system. The data of Fig. 3 is normalized to the H_2O partial pressure to remove this background effect. It is seen that oxygen evolution is not detectable until the sample temperature has reached approximately 560 K even though resistivity and optical density changes indicate that the composition of the oxide alters in the range of temperature above about 520 K.

The introduction of a partial pressure 0.2 torr of hydrogen into the sample chamber during a decomposition experiment had a marked effect on the stability of the oxide films. As shown in Fig. 2, decomposition in the presence of hydrogen, as detected by the reduced sample resistivity, began at about 300 K and by 350 K the oxide had been completely reduced and was exhibiting metallic behaviour.
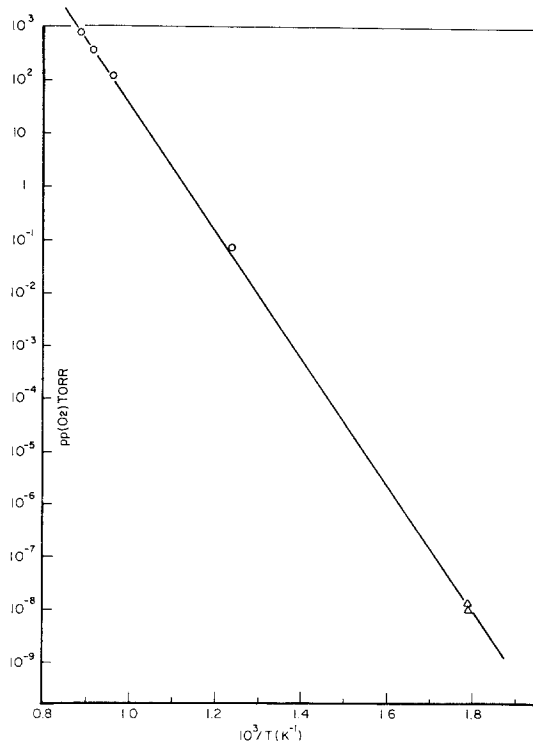
3. Discussion

It has been found possible to produce thin films of PdO of good optical quality by oxidizing sputtered Pd films in either an atmosphere of oxygen or air at 700°C. Optical absorption and photo-conductivity measurements on these films indicate extrapolated optical and photoconductive band gaps of 2.13 ± 0.03 eV and 2.67 ± 0.03 eV, respectively. The difference between these values suggests that the first optical absorption peak may be caused by excitonic transitions. From the temperature dependence of the dark conductivity of the films it is clear that they are heavily doped with shallow traps and that the density of these traps is strongly dependent upon the thermal history of the oxide.

If the PdO films are considered to become unstable at that temperature at which their equilibrium partial pressure of oxygen is greater than the partial pressure of oxygen in the "vacuum" ambient, then the present decomposition data can be compared to the equilibrium dissociation pressure measurements of Bell *et al.* [12]. The present measurements were made with oxygen

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partial pressures some seven orders of magnitude lower than those used by these workers. Fig. 4 shows an extrapolation of the data of Bell *et al.* into this low pressure region and it is seen that the agreement between the two sets of data is good and that an enthalpy of dissociation of -1.17 ± 0.06 eV can be used to describe the dissociation reaction over the complete range of oxygen partial pressures between 1 atm and 10^{-8} atm.

In agreement with the observations of Okamoto and Aso, the presence of hydrogen has been found to greatly reduce the thermal stability of PdO; the films decompose to palladium metal by 350 K in the presence of hydrogen as compared to a temperature of about 580 K in a vacuum ambient.

Acknowledgement

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