JOURNAL OF SOLID STATE CHEMISTRY 3, 314–316 (1971)

Crystal Growth and Semiconductivity of Palladium Oxide

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Received November 20, 1970

A method for growing crystals of PdO by vapor transport is described. Electrical measurements on the product crystals show semiconductivity with a low activation energy that is probably extrinsic. A bonding model consistent with semiconductivity in PdO is proposed.

Palladium oxide, PdO, is a useful catalyst and is an ingredient in certain resistor–conductor compositions utilized by the electronics industry. Consequently, the nature of electrical transport in this oxide is of interest. In previous work on thin films of PdO prepared by oxidation of evaporated Pd films, Okamoto and Aso (*1*) reported resistivities as functions of temperature between 77 and 560°K and Hall coefficients and mobilities at 300°K. Their films were found to be semiconducting and appeared to be characterized by extrinsic, *p*-type conduction at room temperature with a transition to intrinsic behavior at about 500°K. The activation energy for semiconduction in the intrinsic region led to an estimated band gap of about 1.5 eV. Since thin films are difficult to characterize chemically, and since physical properties measured on them may be subject to distortion because of induced strain from the substrate or because of extraneous grain-boundary effects, it seemed desirable to confirm semiconductivity in PdO on single crystals of the material. Crystal growth of PdO is complicated by decomposition of the oxide below the melting point. In this note, we describe a technique that permits crystal growth of PdO by vapor transport and report some of the electrical transport properties of our crystals.

Initially, attempts were made to grow crystals of PdO from a $PdCl_2$ flux in a sealed silica tube. Reagent PdO was obtained from City Chemical Corp., New York; $PdCl_2$ from Fisher Scientific and from Alfa Inorganics. PdO was preheated in flowing oxygen at 800°C, and $PdCl_2$ was dried by heating in air at 300°C. The reagents in approximately equal proportion by weight were placed in a silica tube; the tube was evacuated and sealed; finally, the tube and its contents were heated in a muffle furnace at about 825°C with the tube in an inclined position to maintain the melt at one end. After 48 hr at this temperature, the furnace was slowly cooled at a rate of 10°C/hr. On examination of the cooled system, dark-green, lustrous crystals of PdO, approximately 1 mm on an edge, were found adhering to the *upper* end of the tube completely free of $PdCl_2$ flux. Since a natural temperature gradient in the furnace had resulted in a hotter temperature at the upper end of the tube, it was assumed that crystal growth had occurred by a vapor transport reaction in the direction of the hotter zone. Subsequent experiments confirmed this process and showed the optimum temperature to be about 825°C at the source region (T_1) and 900°C at the growth region (T_2). Under these conditions, PdO could be reproducibly transported in the presence of $PdCl_2$ to provide well-developed, columnar crystals 1–2 mm in size, in times of the order of 2 days.

X-Ray powder patterns of ground crystals obtained from the transport process described above were identical to powder patterns previously reported for PdO. In addition, tetragonal cell dimensions $a_0 = 3.0434 \pm 2$ and $c_0 = 5.3363 \pm 4$, which were calculated by least-squares refinement of data obtained using a Hägg–Guinier camera, were in good agreement with those published by the National Bureau of Standards (*2*). Nominal stoichiometry was confirmed by oxygen analysis using a Leco "Nitrox 6" oxygen analyzer which incorporates inert gas fusion and a gas chromatograph readout (wt % oxygen found $= 13.06 \pm 0.15$; theoretical $= 13.07\,\%$).

TABLE I

RESULTS OF SPECTROGRAPHIC ANALYSES OF PdO CRYSTALS AND STARTING REAGENTS

Nominal composition	Spectrographically detected impurities[a]								
	Pt	Si	Cu	Mg	Au	In	Al	Mn	Fe
PdO (crystal)	15–75	25–150	10–50	2–10	15–75	15–75			25–150
PdO (crystal)	75–350	250–1000	25–150						
PdO (reagent)[b]	10–50	100–500	5–25	20–100			100–500	50–250	500–2500
$PdCl_2$ (reagent)[c]	50–250	20–100	5–25		10–50		20–100		20–100

Nominal composition	Spectrographically detected impurities[a]								
	Na	Ca	Ba	Ni	Pb	Ti	Ru	Cd	Sn
PdO (crystal)									
PdO (crystal)									
PdO (reagent)[b]	200–1000	100–500	50–250						
$PdCl_2$ (reagent)[c]	10–50	10–50		25–150	20–100	20–100	20–100	10–50	25–150

[a] Concentration limits expressed in parts per million.

[b] Obtained from City Chemical Corp.

[c] Obtained from Fisher Scientific.

Spectrographic analysis of the crystals showed the presence of large amounts of cation impurities, particularly platinum (see Table I). The separate analyses shown in the table (rows 1 and 2) for PdO crystals are typical of different sets of results that were obtained depending on the source of reagent $PdCl_2$. The crystal described in the first row was grown using $PdCl_2$ supplied by Alfa Inorganics; that in the second row was grown in the presence of Fisher Scientific $PdCl_2$. In rows 3 and 4, analysis of two of the reagents, City Chemical PdO and Fisher Scientific $PdCl_2$, are given; unfortunately, all of the Alfa Inorganics $PdCl_2$ was consumed in the growth experiments so that analyses of this reagent are not available. Comparison of the analyses for the crystals with those of the reagents indicates that considerable purification occurred during the transport process. Except for platinum, copper and silicon, the original impurities in the reagents are generally missing or are reduced to trace levels after transport. The occurrence of silicon in the analyzed crystal specimens is possibly a result of growth on the walls of the silica reaction tubes. However, it is apparent that platinum and copper are co-transported, and perhaps even enriched by the process.

Electrical resistivities of several crystals were measured as functions of temperature over the range 4.2–300°K using a conventional four-probe technique. It was apparent from these measurements that all crystals were basically semiconducting. However, both the level of resistivity and the activation energies for semiconduction, derived in the usual manner from the slope of a logarithmic plot of resistivity data vs. reciprocal temperature, varied considerably from sample to sample. In addition, the $\log\rho$ vs. $1/T$ plots deviated from linearity below 100–200°K so that activation energies could only be estimated at the higher temperatures. Typical values of resistivity were in the range 10–1000 ohm-cm at room temperature and activation energies were in the range 0.04–0.10 eV. Seebeck coefficients, referred to Cu as a standard and measured across a crystal, one end of which was at room temperature and the other at 50°C, were all positive, indicating that the predominant current carriers were p type.

In view of the large amounts of native impurities present in PdO, the variations in electrical properties are not surprising. The only conclusions that can be safely drawn from our electrical data are that PdO is indeed a semiconductor in confirmation of the work on polycrystalline films of Okamoto and Aso (*1*), that the oxide as normally obtained from reagent-grade chemicals is heavily doped with active acceptor levels at energies from 0.0 to 0.1 eV above the highest filled band, and that these acceptors give rise to extrinsic p-type conductivity.

Confirmation of semiconductivity for PdO is significant. In this respect, PdO joins PtO_2 and Rh_2O_3 as being the only semiconducting normal oxides of the platinum group metals. RuO_2, OsO_2, RhO_2, and IrO_2 are metallic conductors (*3*). All the semiconductors in this group have either d^6- or

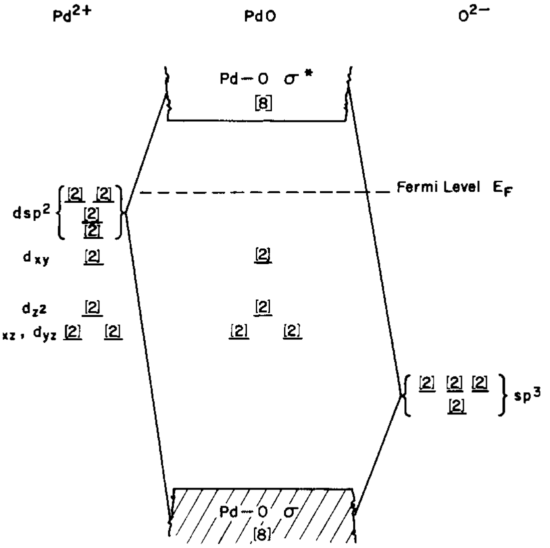

FIG. 1. Schematic, one-electron energy diagram for PdO.

d^8-electron configuration. The d^6 ions Pt^{4+} and Rh^{3+} are in octahedral coordination in their respective oxides, and the six d electrons are just sufficient to completely fill the cationic t_{2g} levels so that the Fermi level occurs in the band gap between the bands of t_{2g} symmetry and those derived from e_g wavefunctions. Palladium(II) oxide crystallizes in a tetragonal unit cell in which both cation and anion are coordinated by four near neighbors of opposite charge (*4*). The oxygen ions are tetrahedrally coordinated by palladium; palladium ions are coordinated by a square-planar array of oxygens. Square-planar coordination is, of course, common for the divalent ions of both palladium and platinum. However, in PdO the planar arrays are actually rectangular, the "square" being elongated slightly in the direction of Pd chains that propagate in directions perpendicular to the c-axis. In these chains the planar arrays share common edges. Assuming that palladium uses essentially dsp^2 hybridized orbitals in bonding to its planar oxygen neighbors, then a schematic molecular orbital diagram analogous to those previously proposed for rutile oxides (*3*) can be constructed for PdO as shown in Fig. 1. In the figure, it is assumed that the palladium $d_{x^2-y^2}$ orbital, which is directed towards neighboring oxygen ions, is involved in dsp^2 σ-bonding to oxygen, which in turn uses tetrahedrally oriented sp^3 orbitals in bonding to near-neighbor palladium ions. The splitting of the remaining d orbitals would be approximately as shown in the central part of the figure. The d_{xy} orbital is spatially oriented towards near-neighbor palladium ions in the chains and the localized "level" shown in the figure may actually be broadened by metallic bonding into a band of collective-electron states. This would seem to be indicated by the relatively high conductivity of p-type PdO. In either event, with eight d electrons per palladium ion this level is normally filled so that the Fermi level would be expected to lie in an energy gap consistent with the observed semiconductivity of PdO.

Acknowledgments

The authors would like to thank Miss M. S. Licis and Dr. J. F. Whitney for assistance in obtaining the X-ray data.

References

1. H. OKAMOTO AND T. ASO, *Jap. J. Appl. Phys.* **6**, 779 (1967).

2. H. E. SWANSON, R. K. FUYAT, AND G. M. UGRINIC, *Nat. Bur. Stand.* (*U.S.*) *Circ.* **4**, (539) p. 27.

3. D. B. ROGERS, R. D. SHANNON, A. W. SLEIGHT, AND J. L. GILLSON, *Inorg. Chem.* **8**, 841 (1969).

4. W. H. ZACHARIASEN, *Z. Phys. Chem.* **128**, 421 (1927).