Semiconductors Produced by Doping Oxide-glasses With Ir, Pd, Rh or Ru

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Abstract

Semiconductors were produced by diffusion doping oxide glasses with more than 1 wt % of Ir, Pd, Rh or Ru and by implanting 40 kilovolt Ir ions into several oxide glasses. Hall mobility at 300° K and 78° K was less than 0.005 cm^2/volt sec. Mobility from impurity concentration and conductivity was 0.001 cm^2/volt sec. Conductivity was not ionic. Enough direct current was passed through one sample to have plated out a million times as many Ir ions as were in the sample with no change in conductivity. X-ray small angle scattering indicates that conductivity was not due to electron hopping between conducting islands. Conductivity was ohmic at 300° K and was field dependent below 4° K. Thermoelectric power of 12 to 25 microvolts per degree relative to copper indicated hole conduction. The material absorbed throughout the visible region. For constant firing temperature and time at a constant oxygen pressure conductivity increased as impurity concentration increased and varied from 10^{-3} to 10^2 reciprocal ohm-cm. For a constant concentration of platinum-metal ions and for equilibrium firing, the conductivity was directly proportional to the oxygen pressure. Firing in hydrogen to remove oxygen reduced conductivity at the rate of two carriers per oxygen atom removed. These data indicate that the frozen-in valence states of the platinum-metal ions serve as the source of the carriers.

Introduction

Oxide glasses were caused to become amorphous semiconductors by heavily doping them with iridium, ruthenium, rhodium or palladium. The conductivity is between 10^{-3} and 10^2 ohms^{-1} cm^{-1}.

Most metals will oxidize, dissolve into and become a part of molten oxide glass. They are so chemically active with oxygen that all of their electrons form binding orbitals. They are unable to retain charges which can act as donors or acceptors. Thus, no one has reported doping oxide glasses with ordinary dopants such as boron, phosphorous, etc.

Certain members of the platinum metal family, while not inert, are relatively inactive chemically. These metals have more than one oxidation state and they can retain charges which contribute to the electrical conductivity.

Conductivity vs. Temperature

Sample resistance was measured as a function of temperature from 1.48°K to 1150°K. For several hundred samples, the d-c resistance was measured by the volt-amp method for about 20 different temperatures between the triple point of nitrogen and 200°C.

Typical data are shown in Figure 1. There exists a striking similarity between the shapes of these graphs and those shown in Pearson and Bardeen's Figure 4A, "Resistivity of Silicon-Boron Alloys as a Function of Inverse Absolute Temperature" (7).
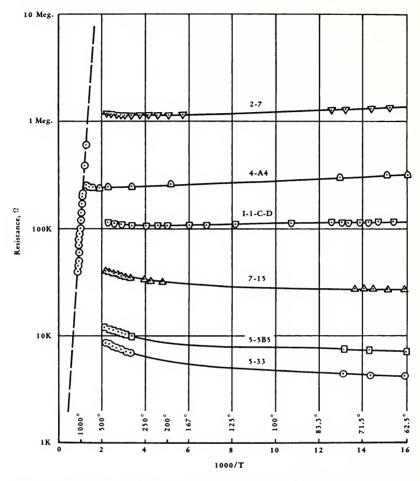
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FIGURE 1. *Logarithm of resistance vs. reciprocal absolute temperature for various con-centrations of iridium in an oxide glass. These curves are typical examples of platinum metals doped into any one of many kinds of oxide glasses.*

At high temperatures the intrinsic resistance of one sample of oxide glass was shown. For low doping and low temperature the resistance is given by $R = A \exp (W/kt)$. For high doping the carriers seem to be degenerate. At low temperature as the doping increases, the slopes of the curves decrease monotonically as far into the "degenerate" region as it was carried.

It is obvious from the shape of these curves that at low doping, the conduction cannot be metallic.

The conduction cannot be ionic because there was no transport of ions. Ionic conduction in glass usually leads to a depletion of ions from

some volume and a change in resistance as current is passed through the unit. Tests of many hours duration on many samples showed that the resistance did not change as much as one part in 10^5 after enough charge had passed through the samples to have plated out a million times as many iridium atoms as were in the sample.

There was no electrolysis of metals nor of oxygen. In some cases the only element common to different samples was oxygen. For example a lead-borate-oxide glass doped with iridium conducted, yet so did an alkali-silicate-oxide glass doped with ruthenium. In every case at least half of the atoms in the system were oxygen. In no case was there any evolution of oxygen at the terminals.

The resistance at 300°K was ohmic over more than 6 orders of magnitude between 100 μv per cm and 500 v per cm. Conductivity did depend on the field below 4°K. The data here are too meager to establish the relationship between conductivity and electric field with accuracy.
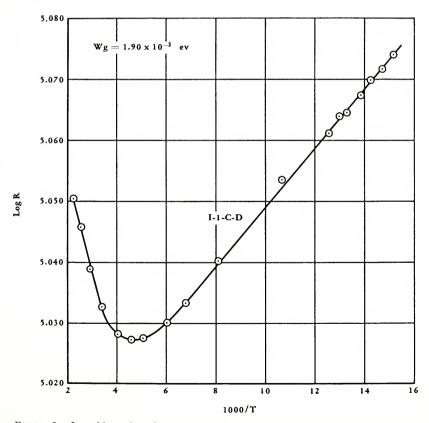

FIGURE 2. *Logarithm of resistance vs. reciprocal absolute temperature for sample I - 1 - C - D of* FIGURE 1. *Note how the experimental points fit a smooth curve even at greatly expanded vertical scale.*

The conduction was not due to electron hopping between conducting islands with dimensions of the order of 100 Å as described by Neugebauer and Webb (6). Many X-ray small angle scattering experiments were performed in search of this effect. In some cases particles of this size were found, but there was no correlation between particle size and resistivity of the sample. Based on their model, Neugebauer and Webb (6) predicted the magnitude of the resistivity and its temperature
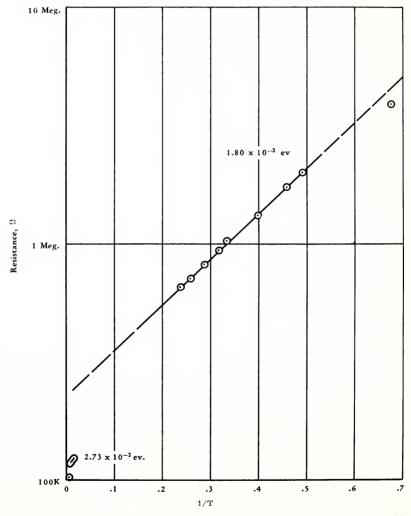

FIGURE 3. *Logarithm of resistance vs. reciprocal absolute temperature for a sample with a room temperature resistance of 100 kilo ohms. The slope of this curve in the liquid nitrogen is 2.73 × 10⁻³ ev. The slope in the liquid helium range appears to be 1.80 × 10⁻³ ev. The point at 1.48° K is below the extrapolated straight line. This probably indicates that the curve is not truly straight anywhere, but drops off continuously as predicted by Mott (5). See text.*

dependence. The resistivity in this study was several orders of magnitude too low to have been due to this effect and the temperature dependence differed from that predicted.

Ir O_2 and Ru O_2 single crystals are metallic conductors (8), but they play no part in the conduction in these Cermets.

The conduction was due to the presence of metals belonging to the platinum family. The glasses did not conduct (that is, the conductivity was many orders of magnitude less) unless these metals were present.

There were no compensating metals present.

Figure 2 is the curve which appeared flat in Figure 1. The points fit a smooth curve and at low temperature the line is straight with a slope of 1.90 x 10^{-3} ev.

Figure 3 shows how one sample behaves at liquid helium temperatures. The resistance of this sample was 10^5 ohms at 300°K. In the liquid nitrogen range the slope was 2.73 milli-electron volts. The curve as drawn shows a slope of 1.80 milli-electron volts below 4°K.

However, the point at 1.48°K is definitely below the curve.

This curve exhibits the fall-off in slope of the ln ρ vs 1/T at low temperature as predicted by Mott (5). Probably at no point is the curve truly a straight line. It appears to fit a straight line over limited temperature ranges, but its slope probably decreases continuously. This change in slope may occur for all of our samples.

Hall Effect

In no sample could a Hall voltage as large as 10^{-9} volts be detected at any temperature. For some samples, 10^{-9} volts would represent a mobility of about 3 x 10^{-3} cm^2 per volt sec. The carrier mobility in all of our samples was less than this amount.

Seebeck Effect

Thermoelectric emf was measured in two ways. In the first method, one end of a long, slender sample was fixed in an ice bath while the other end was heated to various temperatures. In a variation of this method, the cold end was kept in a liquid nitrogen bath.

In the second method, pt-pt 10 rh thermocouples were welded to each end of a Cermet sample about 5 cm long. The sample was inserted to a series of positions of increasing temperature in a tube furnace so that the ends of the sample were at different temperatures. The temperature of each end could be measured. The Seebeck voltage could be measured between the two platinum wires.

In every case, the Seebeck Voltage indicated hole conduction.

Conductivity vs. Metal Concentration

The conductivity as a function of concentration of ruthenium in one kind of glass fired at one temperature for a fixed time in air is shown in Figure 4. Each point on the curve represents five samples. The bars cover the maximum and the minimum resistance of the group. The
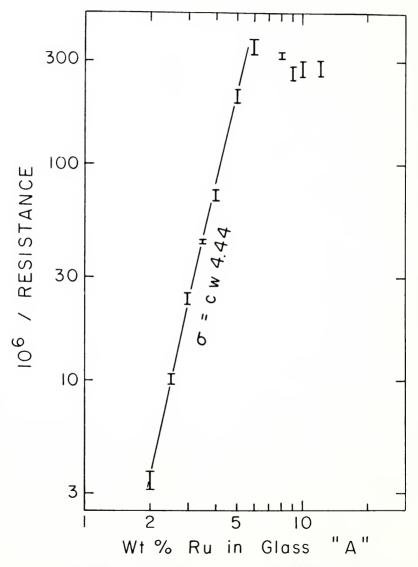

FIGURE 4. *Logarithm of conductivity at 300° K vs. logarithm of weight percent ruthenium in glass A. The Cermets were fired in air through a tunnel kiln so that each sample was exposed to the same temperature-time profile. For these samples $\sigma = CW^{4.44}$ up to about 6 wt% where devitrification occurs.*

curve is fitted by a power law up to the point where devitrification begins. The data will not fit an exponential dependence of conductivity on concentration.

For Glass "A" containing lead, silicon, Cadmium and aluminum oxides, devitrification occurs at about 6 wt % Ru. Devitrified samples look like black emery paper.
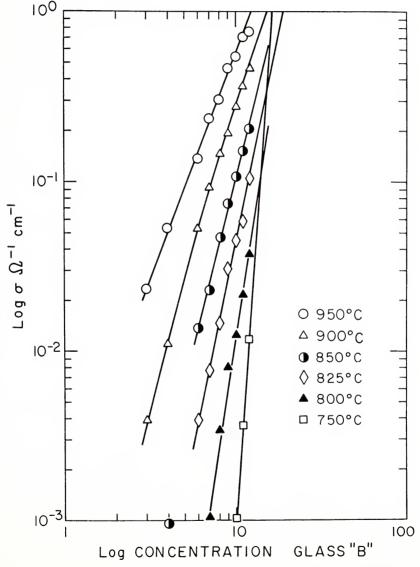

FIGURE 5. *Logarithm of conductivity at 300° K vs. logarithm of concentration of ruthenium in glass B. The samples were fired in air for constant times, but for different temperatures. The exponents of the different curves vary from 2.6 to 13.3.*

For a different glass, labeled B, the effect of varying the firing temperature is shown in Figure 5. Firing time was a constant. Devitrification occurred at higher Ru concentration for this glass.

Resistance vs Firing Time in Air

If the number of metal atoms, the external oxygen concentration and the firing temperature were held constant and a number of similar samples are fired for different times, the resistance appeared to decrease exponentially with time to approach a constant value.

Oxygen Concentration

Figure 6 shows the conductivity of a series of similar samples fired for the same time and temperature at different pressures of oxygen. The arbitrary line with a slope of one drawn on the graph indicates that the
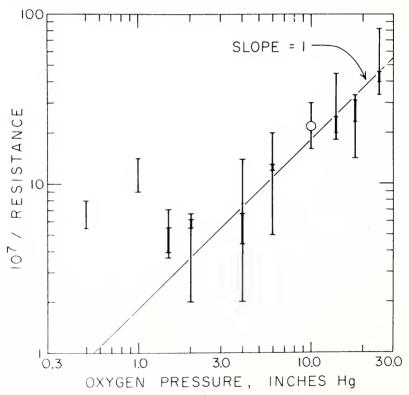

FIGURE 6. *Logarithm of conductivity at 300° K vs. logarithm of oxygen pressure. The samples were fired under a controlled atmosphere of commercial oxygen for a constant temperature and time. The arbitrary straight line has a slope of 1. Each bar on the graph covers the measured range of 10 samples which were not precisely uniform in thickness. Later techniques improved the reproducibility of the sample dimension, but this experiment was not repeated.*

conductivity varied directly as the number of oxygen atoms diffusing into the sample and reacting with the ruthenium.

Firing in Hydrogen

An especially large sample was made for thermogravimetric analysis. A Cermet mix containing 3.60 wt % Ru was screened and fired on a substrate. The measured mass of the sample was 0.303 g and its resistance at 300°K was 23 kilo ohms. The sample was fired in hydrogen for 30 minutes at 500°C.

The sample lost a mass of 760 μg and its resistance at 300°C increased to 704 kilo ohms.

A previous test showed that the hydrogen firing at 500° C did not affect the glass.

At 500°C, apparently hydrogen converted Ru O_2 to Ru_2O_3. The water formed evaporated from the sample. Each Ru O_2 presumably contributes one hole for conduction. Conversion of each Ru O_2 to ½ (Ru_2O_3) or removing one-half of an oxygen atom from each Ru atom removes one
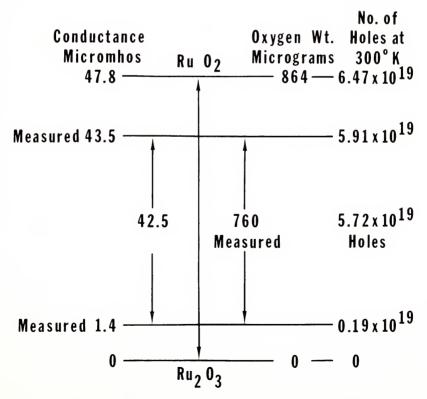

FIGURE 7. *Schematic diagram showing how removal of oxygen from one sample of Cermet removes holes and correspondingly reduces conductance.*

hole thus removing one charged carrier. The Ru in the sample was 3.6% of 0.303 gm or 10.9 mg, or 6.47×10^{19} atoms. The loss of 760 μg of oxygen represented a loss of 2.86×10^{19} atoms of oxygen, or 5.72×10^{19} holes (two holes per oxygen atom removed). The conductance became 1/704 kilo ohms or 1.4 micromhos. The loss in conductance was 43.5 — 1.4 or 42.1 micromhos.

In Figure 7, the quantity of oxygen required to convert $Ru_2 O_3$ to $Ru O_2$ is plotted schematically on the vertical scale. For this sample, which contained 10.9 mg of Ru, 864 μg of oxygen was required for the conversion.

On the left, conductance of the sample in micromhos was plotted, and on the far right the number of holes in the sample at 300°K.

When the sample was originally fired in air, the ruthenium was oxidized to the level such that its measured conductance was 43.5 micromhos. The sample was then fired in hydrogen. This firing removed a measured quantity of 760 μg of oxygen or 5.72×10^{19} holes and reduced the conductance to the measured value of 1.4 micromhos. The assumption that removing 5.72×10^{19} holes removed 42.5 micromhos of conductance gave the scale of the graph. For this sample one micromho was equivalent to 0.1345×10^{19} holes, or 10^{19} holes was equivalent to 7.44 micromhos. Now the measured level of 1.4 micromhos above zero was set to be 0.19×10^{19} holes.

Firing this sample in air at the temperature and time did not oxidize all of the Ru to $Ru O_2$. Only 5.91 to 10^{19} atoms of Ru out of a possible 6.47×10^{19} or 91.3% were combined as $Ru O_2$. The remainder was oxidized only to the $Ru_2 O_3$ level.

For this sample the carrier concentration was 11.2×10^{20} Ru atoms per cm^3 times 91.3% or 10.2×10^{20} holes per cm^3. $\sigma = 0.204 \ \Omega^{-1} \ cm^{-1}$. The mobility $\mu = \sigma/ne = 1.25 \times 10^{-3} \ cm^2/volt \ sec$.

Other Physical Properties

No magneto-resistance was observed up to 14 kilogauss. No photo-conductivity was observed at liquid nitrogen temperatures or above. A very small increase in conductivity was noted when light from an incandescent bulb (microscope illuminator) was focused on a sample bathed in liquid helium. This was attributed to the heating of the sample, not to photoconductivity of the sample. The samples absorbed energy throughout the visible region.

The kind of glass does affect the conductivity, suggesting that the conductivity might be proportional to the square of the dielectric constant. However, in these experiments, the effect of the dielectric constant was not isolated from other effects, particularly that due to the temperature of firing, i.e., that of quenching the oxide into a particular frozen-in valance state. Obviously this latter effect depends on the softening point of the glass.

No effects such as rectification were observed which could be interpreted as due to the contacts or terminations.

Noise was proportional to 1/frequency for these samples at room temperature. The noise was not measured at any other temperature.

An unsuccessful attempt was made to measure mobility directly (2, 3) by injecting carriers and measuring the time to travel a microscopic distance. This experiment indicated the lifetime was very short. If it is assumed that $\mu = \epsilon \tau / m^*$ with $\mu = 10^{-3}$ and $m^* = m$, τ is indeed very small. Smaller values of m^* require even smaller values of τ.

Conductivity in alternating current below 4°K is independent of frequency up to 10 kc/sec.

It is interesting to compare Sb-doped Ge (1) with Ir-doped glass.

I noted that at the doping level just high enough to make Fritzsche's Sb-doped Ge become degenerate, $N = 2.7 \times 10^{17}$ atoms per cm^3, ρ 300 $=$ 0.015 ohm cm and $\mu = 1500$ cm^2/volt sec. At the doping level required to make Ir in glass "degenerate," $N = 1.2 \times 10^{21}$, $\rho = 2.1$ and $\mu = 1.5 \times 10^{-3}$. The ratio of N is about 5000, that of ρ is about 200 and that of μ is about 10^{-6}.

Ion Implantation[1]

Forty kilovolt ions of Ir-193 were implanted into fused SiO$_2$ and five other glasses. The doping levels were 10^{14}, 10^{15} and 10^{16} ions per cm^2. The Lindhard depth of penetration and the deviation of the range for 40 kv Ir-193 into SiO$_2$ were computed by Gibbons and Johnson (4) to be 222Å with a spread of $\sim$ 22Å. The electrical properties of the ion implanted material is about the same as that of the diffused material. If it is assumed that half of the Ir-193 ions do stop in a layer only 45Å thick, if the quantum mechanical effect of such a thin conductor is neglected, and if the conductivity based on the behavior of the same number of ions diffused into the glass is estimated, the measured conductivity is obtained. This is good evidence that the holes do not reflect or scatter from the surface of the conductor and therefore they hop short distances in short lifetimes, Also, the conductivity of the various glasses were crudely proportional to the square of the dielectric constant.

It appears that when the 40 kv Ir ions stop in oxide glass, local heating and other effects permit the ions to form chemical bonds with neighboring oxygen atoms and that Ir introduced by ion bombardment forms the same bonds as Ir diffused into the glass at high temperature.

Discussion

These experiments indicated that each tetravalent atom of one of the platinum metals in an oxide glass can contribute a hole which participates in the conduction mechanism. The trivalent atoms seemed

to take no part in the conduction. The valence state was fixed at high temperature by adding or removing oxygen from the platinum metal ion. When the sample was cooled this valence state was frozen-in. Since the rate of cooling was rapid, this may be considered a quenching effect. The number of platinum metal ions frozen in the tetravalent state determined the number of holes available to carry the current, thus fixing the resistance (or conductance) of the sample. The number of carriers was easily changed by changing the number of atoms in the tetravalent state. This could be done only at high temperatures.

The resistance could be changed by changing the total number of platinum metal atoms in a sample. However, in a sample already manufactured which contains a fixed number of platinum metal atoms, the number of tetravalent atoms could be changed by increasing or decreasing the oxygen content of the sample. This could be done by firing for a different time at a given oxygen pressure and temperature, by firing in an oxidizing or reducing atmosphere or even by firing at a different temperature.

At high temperatures the oxides of the platinum metals were volatile, so only a limited temperature range was available for work.

Under certain conditions semi-conducting glass could be made from osmium. However, osmium oxide was very volatile and poisonous, and it is difficult to process the glass without losing osmium.

In these experiments the conductivity apparently depended on the state of one of the electrons belonging to the d-shell of the platinum-metal atom. If this electron was bound to an oxygen atom, there existed a hole in the d-shell (band?) which may act as a trap or otherwise participate in conduction. If there was no oxygen atom nearby to attract the electron, it occupied its ground state in the d-shell and no hole was available.

The conductivity was a discontinuous function of concentration. If the concentration was less than about 1 wt % or about 3×10^{20} Pt-metal atoms per cm^3 the sample conductivity decreased by many orders of magnitude to that of the intrinsic conductivity of the glass. At this concentration the average volume occupied by only one ion was about 3×10^{-21} cm^3. Thus, at the average distance between ions of about 15Å, the samples change from the conducting to the non-conducting state.

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