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CRYSTAL CHEMISTRY OF DEFECTIVE STRUCTURES IV - CHANGE OF A P-TYPE SEMICONDUCTOR INTO A N-TYPE SEMICONDUCTOR BY VAPOR TREATMENT

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CRYSTAL CHEMISTRY OF DEFECTIVE STRUCTURES IV

CHANGE OF A P-TYPE SEMICONDUCTOR INTO A N-TYPE SEMICONDUCTOR BY VAPOR TREATMENT

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ABSTRACT

Cuprous oxide, Cu_2O, which has been grown on metallic copper by low temperature oxidation represents a P-type semiconductor. The substitution method which has been described previously in detail made it possible to change this cuprous oxide into a N-type semiconductor by exposing it to HCl or $CuCl_2$ vapor at 300°C. The suitability of such an anion substitution (replacing an occasional O^{2-} ion by a Cl^- ion) should be investigated for producing transistors. The method may lend itself to the printed circuit technique, because no high temperatures are involved.

The most convenient method of determining the character of a semiconductor is to combine it with a metal (platinum) and use this combination as a thermocouple. At the hot junction of such a metal-semiconductor thermocouple electrons flow from the metal to the semiconductors if the latter is of the N-type. P-type semiconductors give thermoelectric effects of the opposite sign, i.e., at the hot junction electrons flow from the P-type semiconductor to the metal.

Using the thermoelectric method as a tool it could be demonstrated that, indeed, exposure of a Cu_2O film which had been deposited on copper to the vapor of CuCl at 300°C changed this oxide from a semiconductor of the P-type to one of the N-type.

$$Cu^{+}_{2-x}(+)_x\,(C.V.)_x\,O^{2-} + y\,Cu^{+}\,Cl^{-} = Cu_2^{+}\,(e)_y^{-}\,O_{1-y}^{2-}\,Cl_y^{-} + y\,Cu^{2+}\,O$$

P-type N-type

Strips of metallic copper 1/2" wide and a few inches long were used for the experiments. It was observed that in contact with a hot platinum junction (platinum shoe on a soldering iron) electrons passed from the clean copper surface to the platinum which corresponds to the normal behavior of a Cu metal - Pt metal thermocouple.

(a). The metal was oxidized in air at a temperature sufficient to form the black oxide: CuO. In contact with hot Pt electrons were found to flow from the oxide to the metal: P-type semiconductors.

(b). Exposure of the black oxide to HCl vapor at 300°C caused the color to change from black to red; the E.M.F. dropped very strongly, but still the red oxide retained its P-type conductor properties.

(c). Oxidation of the metal to the red oxide Cu_2O by exposing it to air at a lower temperature produces the normal P-type conducting cuprous oxide, Cu_2O, as one would expect.

(d). Exposure of the Cu_2O film to $CuCl_2$ at 300°C produces a film which gives a high E.M.F. with the hot platinum. This time, however, the electrons flow from the platinum across the hot junction to the oxide film: this means that the cuprous oxide had been changed into a semiconductor of the N-type.

No quantitative measurements of the E.M.F. were attempted, as the purpose of these experiments was only to prove that it is possible to change the type of a semiconducting oxide by exposing it to vapors at relatively low temperature. The treatment of a Cu_2O semiconductor of the P-type on copper with either HCl, CuCl or $CuCl_2$ causes a reduction. Chemically speaking, the number of Cu^{2+} ions in such a P-type Cu_2O decreases and Cu^{+} ions change into Cu° atoms. As one would expect from a material containing elemental copper in a finely subdivided form, it will oxidize on prolonged exposure to the atmosphere. Indeed, the N-type conductor was found to deteriorate with time and gradually convert back into a P-type conductor.

It would, no doubt, be worthwhile to make a more intensive study of reactions between semiconductors and vapors, especially in connection with printed circuit techniques. The fact that exposure of an oxide to certain metal halides in vapor form can change the character of a semiconductor may well find technical applications similar to those of the better known germanium transistors.

REFERENCES

1. W. Capps and W. A. Weyl. Techn. Report No. 26 of this series.

2. G. H. Johnson and W. A. Weyl. Techn. Report No. 25 of this series.

3. (a). J. Bardeen and W. H. Brattain

Phys. Rev. 74 230 (1948)
74 231 (1948)

(b). W. C. Dunlap, Jr. Research Laboratory Reprint No. 1595 General Electric Company.