SEMICONDUCTING CUPROUS OXIDE

THE semiconductors of interest in communication electronics are cuprous oxide, selenium, germanium and silicon, and the Presidential Address of Dr. K. R. Dixit to the Section of Physics* dealt with the work done by him and his collaborators on cuprous oxide since 1930.

The cuprous oxide layers first prepared by him acted as rectifier with a rectification greater than 50. A study of their structure by the method of electron reflection showed two or three diffuse rings outside the shadow edge. The interpretation of these rings was, however, difficult at that time. In 1939, after the publication of papers by Mott, Schottky and Davydov, it became clear that impurities should play a dominant role in semiconductor action. At that time it was the general belief that if impurities are present in the copper block on which the cuprous oxide rectifier is to be based, the rectification would be adversely affected. But it was found that the rectification improved by a factor of 3 if a small amount of silver is included in the copper. Later on, the effect of the admixture of other metals with copper was investigated, and in many cases it was found that the rectification improved.

The study was again resumed in 1952, and the properties of the oxides of copper formed at atmospheric pressure and also at low pressures were investigated. It was found that at atmospheric pressure and low temperature a thin film of Cu_2O is formed. As the temperature and time of formation increases, the crystallites of Cu_2O increase in size and get oriented. With a further increase of temperature and time, they gradually change over to CuO, first showing a three ring pattern, then a definite orientation and finally a fibrous structure. At temperatures beyond 750° C. and with a proper time of formation, it is possible for a Cu_2O film to be formed below the CuO film. Such a composite film shows considerable rectification. At 410° C. and pressures upto 75 mm. of Hg only Cu_2O can be formed. Oxides formed at pressures upto 5 mm. of Hg and a time of oxidation sufficiently long show a peculiar undergrowth structure of Cu_2O in contact with the copper block. This oxide shows four rather broad rings which approximately correspond to 111, 222, 333 and 444 rings of Cu_2O.

The oxides of copper formed at an air pressure 0·5 mm. of Hg in the temperature range 200° C. to 1,030° C. and the effect of subsequent heat treatment on the properties of these oxides have also been studied. It was found that cuprous oxide films formed at 500° C. just begin to show rectification, which becomes appreciable at about 800° C., and increases afterwards very rapidly with the temperature of formation. The appearance of an appreciable amount of rectification is accompanied by a peculiar change in the electron and X-ray patterns. The electron diffraction pattern is now characterised by the 222 ring of Cu_2O becoming broad and strong at the centre, ultimately changing over to a four-arc pattern, showing four rather broad arcs which approximately correspond to 111, 222, 333 and 444 arcs of Cu_2O. The corresponding X-ray pattern is characterised by a weakening of the 200 ring which is normally strong and by an increase in the intensity of the 220 ring. This indicates a change of crystal structure accompanying rectification. The greater the magnitude of rectification the more prominent becomes the change.

Measurement of magnetic susceptibilities shows that as the rectification increases, the film becomes less and less paramagnetic, and ultimately when rectification has increased appreciably it begins to show a definite diamagnetism. The maximum values of rectification are obtained for a rate of cooling of about 3° C. per minute. Such films show a diamagnetic susceptibility of about *minus* 9×10^{-8}. Further suitable heat treatment of these rectifiers reduces their rectification, and increases the diamagnetic susceptibility still further.

Based on these experiments, it is now possible to give the following picture about the formation of a Cu_2O rectifying layer. During the process of formation of a film of Cu_2O at low pressures and high temperatures, a definite number of extra oxygen atoms (very probably about 3) gets associated with a crystallite. This association gives rise to a modified form of crystal structure of Cu_2O, namely, a crystal structure of the zinc blende or the diamond type. During the process of annealing, the oxygen gas is gradually ejected out. This reduces the average number of oxygen atoms associated with a crystallite ($3 \to 2 \to 1$). The maximum rectification is obtained when one atom of oxygen (of course, as an average) is associated with a crystallite of Cu_2O. A further reduction in the amount of oxygen reduces

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the rectification, till we reach the stage of zero oxygen atom associated with a crystallite. This is of course the stage when we have pure Cu_2O which, as is well known, is not a rectifier. It is significant that when we succeed in removing all the oxygen from the rectifier film by suitable heat treatment, the substance is no longer a rectifier, and the crystal structure as shown by electron diffraction changes back from the zinc blende pattern to the normal Cu_2O pattern.

AIR POLLUTION IN RELATION TO PLANT DISEASES

THE Presidential Address of Dr. S. N. Das Gupta to the Section of Botany* dealt with the present status of researches on air pollution in relation to plant diseases, and a brief reference was made to certain aspects of the problems in India which assume special significance in view of the increasing threat of air pollution from programmes of industrial expansion launched under the two successive Five-Year Plans.

Consumption of fuels (specially coal) and other raw materials in industrial plants results in the discharge of smoke and other effluents into the atmosphere causing air pollution. The more important pollutants are sulphur dioxide, fluorine, ethylene, illuminant gas, carbon monoxide, hydrogen chloride, hydrogen sulphide, oxides of nitrogen, unsaturated hydrocarbon, soot and tar in various proportions depending upon the source materials. These are present in the atmosphere in three different phases: (1) gaseous phase, (2) aerosol phase ($0{\cdot}01$-$50\,\mu$), and (3) particulate matter. Of these the gas phase is more common and is the usual toxic phase.

Air pollution is most acute in industrial towns and larger cities. Normally diluted by air current the effluents spread out but under certain meteorological conditions these remain suspended in the atmosphere and attain a concentration which is toxic even in short exposures. Apart from slow poisoning, some of these gases in excessive doses produce acute respiratory trouble in man causing death. Animals also are affected. Effluents in high dose are known to have destroyed vegetation. Some of the pollutants can affect the plants at an infinitesimal dose (1 part in a million and even less). Often these minute doses cause only epinastic or similar reactions and for severe injury (lesions) higher doses are required.

Each gas evokes a characteristic syndrome in plants, but under certain conditions depending upon the species affected and the growth environment, the symptoms become more or less indistinguishable. The gases cause injury to wide variety of plants belonging to the various taxonomic groups, and of different habit and growth form. These include, among others, conifers, spruce, fir, larch, elm, poplar, cedar; mango, banana, citrus, grape, apple, peach, plum and other fruit trees; tomato, potato, brinjal, carrot, bean, radish, sweetpeas, cucumber, lettuce and other vegetables; many ornamental plants like rose, marigold and gladiolus; and also such economic crops as wheat, barley, oat, rye, corn and cotton.

While species differ in susceptibility, the varieties within a species also show difference in susceptibility. The reaction of each species and variety is different in reference to the type of gas employed. For example, alfalfa which is most susceptible to sulphur dioxide is not equally susceptible to fluorine; it is gladiolus which is most sensitive to fluorine. The plants on the basis of their reactions to gas-exposure under controlled conditions can be arranged in order of their susceptibility to a particular gas.

The incidence and extent of air pollution injury to plants are conditioned by the concentration of the toxic agent in the atmosphere, the maturity and the nutritional state of the exposed plants and environmental conditions like temperature, light, soil, moisture, etc.

The susceptibility to disease has been correlated with the condition of the stomata through which the gases enter the leaf tissue. Physiological factors regulating stomatal movements also govern susceptibility of individual plants. Generally speaking, young, vigorously-growing and highly functional leaves are most susceptible, followed by older ones, and most resistant are the youngest leaves. Plants that close stomata in night are more resistant at night than in the daytime. Plants in which stomata are always open (*e.g.*, potato) are equally susceptible in day and night. Plants fully turgid are more susceptible. The near-wilting condition induces resistance. Resistance is high at a temperature below 40° F. and sometimes above 100° F. Sublethal concentration of sulphur dioxide and other gases has no

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