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ELECTRICAL CONDUCTIVITY OF PRISTINE AND HALOGEN-DOPED POLYCRYSTALLINE TUNGSTEN DISULFIDE†

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ABSTRACT Polycrystalline tungsten disulfide is shown to be an electrical semiconductor with a moderate resistivity in the pristine state. Doping tungsten disulfide with bromine and iodine produced electrical semiconductors with energy gaps of 1.2 and 1.1 e.V., respectively. The major charge carrier is negatively charged, i.e., both $WS_2Br_{0.1}$ and $WS_2I_{0.1}$ are n-type materials.

INTRODUCTION

In the past 25 years, many layered transition metal compounds have been shown to exhibit semiconducting properties. However, in a review of the literature for semiconductor properties of tungsten compounds, it was found that little had been done with these compounds[1-7]. One of the simple compounds of tungsten is the disulfide, which has been shown to be a p-type semiconductor when single crystals were doped with As[8-9]. More recently Baglio et al have prepared both the p-type material[10] and the n-type material[11] as single crystals for use as electrochemical photocathodes and photoanodes. To date, however, there has been no reported work on the semiconducting properties of polycrystalline WS_2.

Tungsten disulfide has a $2H_1$ layer structure (MoS_2 structure, space group $P6_3/mmc$) in which the repeating unit is a sandwich

consisting of a hexagonal sheet of tungsten atoms between two hexagonal sheets of sulfur atoms. The stacking in the sandwich is such that the sulfur sheets are superposed and the tungsten position is shifted so as to put each tungsten at the center of a trigonal prism formed by six sulfur atoms[12]. The dominant forces between these sandwich-like layers are presumed to be the relatively weak ones between the sulfur atoms of adjacent layers. This leads to properties similar to those of graphite[13]. WS_2 and the non-isostructural TiS_2 and TaS_2 are layered compounds, which can include dopants between the layers to form inclusion compounds. These inclusion compounds have been reviewed extensively[4-7,14,15]; in their crystal structure, the third dimension (normal to the layer) increases to accommodate the guest molecule. In WS_2 this dimensional increase most probably would occur between the sulfur-sulfur layers.

Moreover, there is a potential technological interest in such compounds. The transition metal dichalcogenides similar to WS_2, i.e., isostructural to MoS_2, are all semiconducting, but intercalation of alkali and alkaline earth metals into the MoS_2 structure yields metallic and superconducting compounds with critical temperatures, T_c, of the order of 7 K[6,8,9,16,17]; also, the Chevrel-type phases $M_xMo_6X_{(8-y)}$ superconduct with T_c of the order of 15 K[18-22].

EXPERIMENTAL

The tungsten disulfide used in this study was obtained in powdered form from Alfa Inorganics Inc. with a stated purity of 99.5%. The bromine and iodine used in this study were Reagent Grade with a purity > 99.9% and were obtained from MCB, Inc. All chemicals were used without further purification.

The WS_2 polycrystalline pellets were made by introducing a weighed amount of WS_2 into a die, evacuating the die to 10^{-3} torr, and compressing the WS_2 at 10,000 psi in a Carver laboratory press. The resultant pellets were 1.25 cm in diameter by 1 mm in thickness.

The doped pellets were prepared by adding weighed amounts of bromine and iodine to a WS_2 pellet in a sealed Pyrex vessel. The WS_2 pellet and the doping agent remained in contact until all of the doping agent was absorbed by the pellet, two to four days. Doping by this method resulted in approximately 5 mole% uptake of Br_2 or I_2 in the WS_2 pellet.

Resistivity measurements were carried out using the four-point probe method[23-24]. Silver contact points on the WS_2 pellet were vacuum vapor-deposited onto the surface of the pellet. The four-point probe resistivity unit with the sample in place was contained inside a Andonian Cryogenic chamber which could be operated between 120 K and ambient temperature. Cooling was done using nitrogen gas "boil off" from liquid nitrogen. The temperature inside the cryogenic chamber was monitored by a copper-constantan thermocouple in contact with the WS_2 pellet. A 150 V potential at 1.40×10^{-6} ampere constant current was applied to the outermost probes; the current was monitored with a Keithley 425A ammeter. The voltage was measured on the two innermost probes with a Keithley 610C electrometer. From the measured current flow and the measured voltage, the resistance was determined. For the system used in this study, the resistivity, in ohm-cm, was equal to 18.85 times the resistance.

The field emission part of the study was carried out by vacuum vapor-depositing through a mask three silver bars onto the WS_2 pellet surface, with a distance of 2 mm between bars. A dc potential was applied to the outer two bars; the center bar was

kept at a negative bias. The current flow between the two outer bars was measured using a Keithley 425A ammeter as a function of the negative bias voltage.

RESULTS

Although the application of the four-point probe resistivity method is strictly only valid for single crystal samples, its application to polycrystalline samples does provide, at least, qualitative data. The resistivities reported in this study probably do not represent the true resistivity, but contain interparticle compaction resistivity contributions. Nevertheless, it is hoped that the variations of resistivity with temperature are intrinsic.

The resistance as a function of temperature in all cases increased as the temperature was decreased, Also, a tailing off was noted below 160 K. These observations indicate that WS_2, $WS_2Br_{0.1}$ and $WS_2I_{0.1}$ are semiconducting. A plot of the logarithm of the conductivity versus the reciprocal of the temperature gave the results shown in Figure 1. In the case of the bromine and iodine doped WS_2, the results are typical of what is observed for semiconductors. The steep part of the curves in Figure 1 near room temperature gave the gap energies, E_g, shown in Table I. These were obtained from the formula $C = C_o \exp(-E_g/2kT)$. The error in the determination of E_g is estimated at plus or minus 0.2 e.V. When a material is insulating or semi-conducting, the resistance of the interparticle contacts will be much less than the resistance of the individual particles of the sample. As a result the measured activation energy should be an accurate measure of the intrinsic gap of the material[26].

The results obtained for WS_2 doped with bromine or iodine agree reasonably well with the intrinsic energy gap measured for a

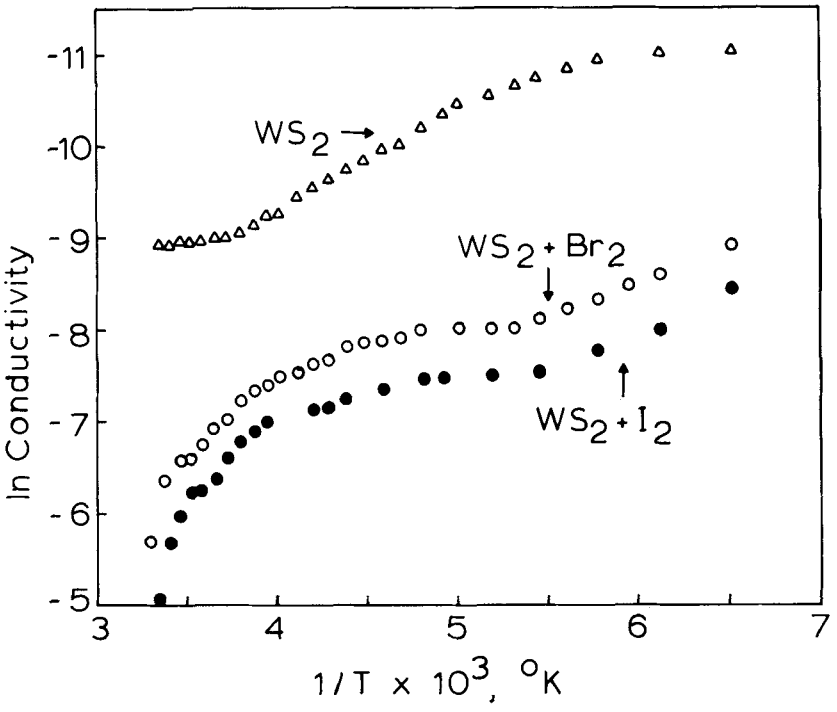

FIGURE 1. The variation of the ln of the conductivity with 1/Temperature.

TABLE I Intrinsic energy gap for tungsten disulfide.

Physical Form	Cond., mho-cm†	Dopant	E_g, e.V.
Polycrystalline	1.3×10^{-4}	Pristine	---
Polycrystalline	17.4×10^{-4}	Bromine	1.2
Single Crystal	---	Bromine	1.3*
Polycrystalline	62.4×10^{-4}	Iodine	1.1

† Measured at 298 K. * Reference 11.

single crystal of WS_2 doped with bromine[11], as shown in Table I. The behavior of the pristine WS_2 with temperature shown in Figure 1 is completely different from the doped material and is not understood at this time. However, since all temperature runs were carried out under the same conditions, i.e., heat lag, etc. would effect the results the same in all cases, the differences observed in the curves are believed to be real.

As the next step in the examination of these materials, their current-voltage characteristics were measured using pellets having three silver bars vacuum vaporized onto the flat surface, with only the two outermost contacts being used. Applying a dc potential to these contacts, the current flowing through the pellet was measured as a function of the applied voltage. The results are shown in Figure 2. The variation of current with voltage was found to be reproducible and rapid. Doping WS_2 with either bromine or iodine produced, within experimental error, identical current-voltage relationships. At 1 VDC the doped samples gave approximately the same current as the pristine material. However, at 29 VDC, the doped material showed a current twice that of the undoped samples, 0.55 micro-amps for the doped material compared to 0.27 micro-amps for the pristine material. The increased current flow in the doped versus the undoped samples was most probably due to an increase in the number of charge carriers.

In order to determine the nature of the charge carrier and whether or not this material would function as a Field Emission device, a negative bias voltage was applied to the center bar in the three bar arrangement on the flat surface of the pellet. Application of a variable negative bias voltage to WS_2 doped with iodine (at an applied voltage of 29 VDC to the outside contacts) results in a current drop of 0.2 micro-amps over the range of bias

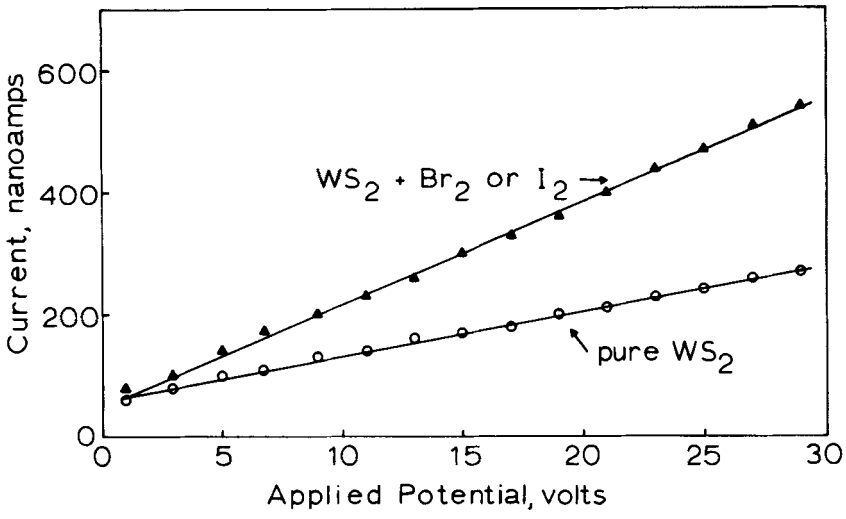

FIGURE 2. The variation of current with applied potential for pure WS_2, $WS_2Br_{0.1}$ and $WS_2I_{0.1}$.

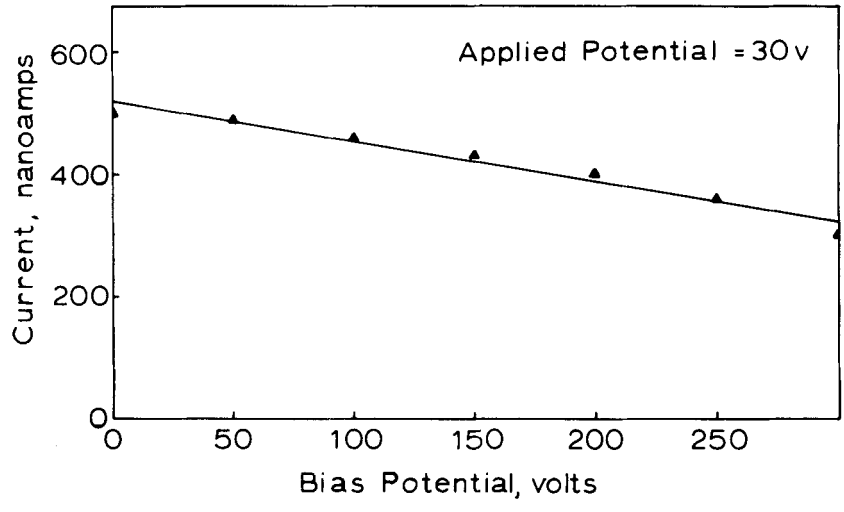

FIGURE 3. The variation of current with negative bias potential for WS_2 doped with Iodine.

voltage from 0 to 300 V, as shown in Figure 3. Voltages above 350 V result in electrical breakdown. Approximately the same results were obtained with WS_2 samples doped with bromine. Both of these systems were completely reproducible and rapid with changes in either the applied voltage or the negative bias voltage on a very short time scale. The preliminary results indicate that doped WS_2 can function as a Field Emission type controller for small currents, and that the charge carrier is negative, i.e., $WS_2Br_{0.1}$ and $WS_2Br_{0.1}$ are n-type semiconductors. This is in agreement with the work of Baglio et al.[11] on bromine doped single crystals of WS_2.

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