Radioactive Doping of Cadmium Sulfide Films and its Effects on Chemisorption

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The purpose of this paper is to demonstrate the continuous impurity doping of a semiconductor with the transmutation products of the decay of a radioactive isotope and to show that this doping predictably influences the electrical conductivity, Seebeck effect, and rates of chemisorption. By this technique the Fermi level of a semiconductor catalytic material could be altered over a wide range in a predictable manner without having to manufacture a new catalyst.

Thin films of CdS containing radioactive S^{35} were studied during the course of the beta decay of S^{35} to stable Cl^{35}. During this decay the electrical conductance increased with time in some cases by a factor of more than 100. External irradiation of non-radioactive films with S^{35} betas of comparable intensity caused some similar effects but of much smaller extent. The greater effect in the radioactive case was attributed to the build up of donor-type Cl^{35} atoms introduced substitutionally into the lattice by the nuclear decay. Both the Cl^{35} build-up and the beta radiation caused an increase in the Fermi level which was found to inhibit the rate of ionized hydrogen adsorption in proportion to the degree of Fermi level elevation.

The proper type of heat treating can reverse the effects of both the radioactive doping and the external radiation. This offers the possibility of adjusting the Fermi level to any desired position in the same semiconductor catalyst.

INTRODUCTION

The large changes which can be induced in semiconducting materials by minute additions of impurities to the lattice suggest the prospect of controlling these changes for a single sample by introducing the impurities at a known continuous rate as the decay products of a nuclear reaction. If the radiation damage accompanying nuclear decay can be kept small, the only appreciable change in the lattice is the random introduction of impurities. When the specific activity of the radioactive isotope is known at one time, the exact number of impurities introduced by the decay can be

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calculated at any later time. Continuous observation of a single radioactive sample should be useful in a study of semiconductor catalysis because the surface chemical properties can then be studied as a function of doping without the necessity of changing samples and, therefore, surfaces. It was with this use in mind that this work was undertaken.

A form of radioactive doping was studied first by Lark-Horowitz (1), who irradiated n- and p-type germanium with neutrons and showed that the resulting current carrier concentration changes could be accounted for by the introduction of transmutation impurity atoms. Cleland and Crawford (2) later ascertained that some of the changes induced in the electrical properties of InSb by neutron bombardment were due to the build-up of tin impurities which were transmutation products of the reaction be-

tween In and neutrons. Considerable work was done more recently on transmutation doping of reactor-irradiated silicon and germanium (3–5), especially in connection with producing semiconductor devices (4, 5). All of these experiments involved neutron irradiation of the specimen resulting in considerable damage to the lattice.

In the work reported here the radioactive isotope was introduced directly into the semiconductor during its manufacture. The material studied was CdS in the form of thin films. The radioisotope incorporated into the films was S^{35}. The impurity introduced by S^{35} is Cl^{35} which is a donor-type impurity in CdS (6, 7). The half-life of the decay is 87 days. Since the only radiation is the relatively weak 0.167 Mev beta emitted by S^{35}, the radiation damage should be slight. Electrical conductance and Seebeck coefficient, and rates of ionized H_2 adsorption were measured during a period of several months, over the temperature range 25° to 450°C, to show the effect of the radioactive doping.

In addition to radioactive CdS containing S^{35}, nonradioactive CdS films bombarded externally with S^{35} betas were also studied for comparison.

EXPERIMENTAL

Film manufacture. CdS films were made by reaction of H_2S with thin films of vacuum-deposited cadmium metal. Radioactive films were prepared using radioactive H_2S^{35}. Two different types of film substrate were used. One of these was the inside surface of Vycor glass tubes while the other was the slightly roughened surface of flat fused quartz plates. The most apparent difference in the two types of films was in the grain size but in spite of this, the behavior of each was qualitatively very similar. X-ray analysis showed that the sulfide films were polycrystalline with hexagonal structure.

On the Vycor substrates, cadmium was deposited in a vacuum of 10^{-6} mm Hg over and between two platinum band electrodes spaced 1 cm apart on the inside of Vycor glass tubes. During deposition the tube was kept at dry ice temperature to obtain a uniform film. The cadmium was degassed and then sulfided by contacting with excess H_2S at temperatures from 350° to 400°C. Further details of the film preparation on Vycor are given by Fulkerson (8).

The quartz substrate films were prepared by depositing cadmium at liquid nitrogen temperatures on the slightly roughened surface of flat quartz plates ½ inches wide, 1½ inches long, and $1/16$ inch thick. After degassing, these metal films were also sulfided by contacting with excess H_2S at temperatures from 380° to 400°C. Further details of the manufacture of this type of film are given by Hearn (9).

Both types of sulfided films were degassed after sulfiding by heating at about 350°C for a few hours in a vacuum of from 10^{-6} to 10^{-8} mm Hg to remove excess H_2S. Microscopic examination indicated that the grain size of the films made from cadmium deposited on Vycor at dry ice temperature was considerably larger than the grain size on the quartz, where the cadmium was deposited at liquid nitrogen temperature. The cadmium used was obtained from the American Smelting and Refining Company at a purity specified as 99.999% Cd. The H_2S for the nonradioactive films was Mathieson purified grade specified as 99.5% pure and was dried over Dehydrite before use. Radioactive H_2S was from the New England Nuclear Corporation and the Volk Radiochemical Company at an initial activity of about 10 millicuries/mg of gas. The purity of the radioactive H_2S^{35} was greater than that of the nonradioactive H_2S.

Table 1 gives some comparative information about six films selected for discussion in this paper. As listed in Table 1, these films are referred to by an abbreviated code indicating the substrate and type of preparation. For example, the two radioactive films on quartz are specified as "Rad.-Quartz-1" and "Rad.-Quartz-2." These six films are not the only ones studied in obtaining the conclusions reached here. They are, however, typical examples.

Electrical measurements. Electrical conductance of the films was measured with a Wayne Kerr Universal Bridge B221, oper-

TABLE 1
SUMMARY OF FILM PROPERTIES

Film type	Film age (days)	Chlorine atom concentration $n \times 10^{-18}$ (number/cc)	Temperature T (°K)	Thermoelectric power $-QT$ (ev)	Apparent conduction electron concentration		Conductance (μmho)
					$n \times 10^{-18}$ (Number/cc) for $Q' = 2k/e$	$n \times 10^{-18}$ (Number/cc) for $Q' = 4k/e$	
Rad.-Vycor	313	3.84	400	0.186	0.21	1.4	0.95
Area = 19 cm²			450	0.204	0.28	2.0	5.0
Thickness = 0.48 microns			500	0.215	0.44	2.9	18
CdS wt = 4.4 mg			550	0.227	0.61	4.0	50
Non-Rad.-Vycor	54	0.0	400	0.389	0.00059	0.0043	0.007
Area = 19 cm²			450	0.412	0.0013	0.0086	0.070
Thickness = 0.75 microns			500	0.436	0.0026	0.019	0.41
CdS wt = 6.9 mg			550	0.446	0.0060	0.045	1.7
Rad.-Quartz-1	8	0.50	500	0.273	0.11	0.815	0.44
Area = 3.3 cm²	26	0.88	500	0.191	0.75	4.7	1.6
Thickness = 1.5 microns	33	1.01	500	0.184	0.87	5.4	2.1
CdS wt = 2.5 mg	53	1.41	500	0.170	1.2	7.0	5.4
	82	1.90	400	0.134	0.95	5.3	0.68
	82	1.90	450	0.142	1.3	7.4	2.8
	82	1.90	500	0.154	1.7	9.2	8.5
	82	1.90	550	0.166	2.4	11	17
	110	2.25	500	0.152	1.8	9.5	14
Rad.-Quartz-2	5–8	0.34	500	0.362	0.015	0.11	0.13
Area = 3.3 cm²	23	0.70	500	0.264	0.14	1.0	0.57
Thickness = 1.1 microns	67	1.49	500	0.229	0.36	2.1	2.2
CdS wt = 1.8 mg	74	1.59	500	0.222	0.37	2.5	2.2
	95	1.85	400	0.185	0.24	1.5	0.13
	95	1.85	450	0.198	0.34	2.2	0.77
	95	1.85	500	0.212	0.46	3.1	3.0
	95	1.85	550	0.223	0.67	4.3	9.5
Ex.-Irrad.-Quartz	5–7	0.0	500	0.377	0.010	0.075	0.023
Area = 3.3 cm²	91		400	0.306	0.0068	0.048	0.0032
Thickness = 0.87 microns	91		450	0.307	0.020	0.15	0.025
CdS wt = 1.5 mg	91		500	0.308	0.052	0.37	0.13
	91		550	0.302	0.13	1.0	0.46
Non-Rad.-Quartz	154	0.0	400	0.334	0.0029	0.021	—
Area = 3.3 cm²			450	0.352	0.0064	0.047	0.0018
Thickness = 1.4 microns			500	0.366	0.013	0.097	0.010
CdS wt = 2.2 mg			550	0.367	0.034	0.24	0.043

ating at a frequency of 10 000 radians/sec. The Seebeck voltage was measured with a Cary Model 31V Vibrating Reed Electrometer with output coupled to an Applied Physics Corporation Automatic Multiple Range Recorder, Model 39. This equipment was checked periodically against calibrated resistors and voltages. The input impedance of the electrometer was very high compared to that of the films so that the measurements were effectively made at zero current conditions.

Although an isolated beta emitter will build up a total positive charge due to negative particles leaving during the decay, the films were all grounded in the course of making the electrical measurements so that they were not measured at any absolute potential above ground.

The temperature differentials for the Seebeck coefficients were measured by thermocouples attached to each end of the films using a Leeds and Northrup Model 8686 Millivolt Potentiometer. External heaters were used to produce the temperature gradient. Since CdS is often a photoconductor, the films were shielded from room light. The conductance of the films at all temperatures, above room temperature, was much greater than the conductance of either the Vycor tube or the quartz plate substrates. This was checked by blank runs on substrates with no film. Except when the effect of adsorbed gases was being studied, all electrical measurements were made in vacuum at pressures from 10^{-5} to 10^{-9} mm Hg. No variation in film properties with vacuum level was detected.

For these vacuum studies conductance and Seebeck coefficient were usually measured at temperature intervals while the films cooled from the degassing in vacuum at 300°C which preceded each set of measurements. Between each set of measurements made during cooling, the films were kept evacuated at room temperature.

External irradiation experiments. To determine the effect on film electrical properties of the beta radiation itself during the radioactive decay, several nonradioactive quartz plate films (designated Ex.-Irrad.-Quartz) were irradiated externally by the S^{35} beta flux from specially prepared radioactive CdS^{35} films held opposite the nonradioactive film. Only the region of the film between the electrodes was irradiated. The radioactive source film was made thick enough so that the beta flux incident on the irradiated film was approximately equivalent to the total beta emission which would have been produced had the irradiated film been radioactive. For the film Ex.-Irrad.-Quartz discussed here the initial external beta flux was equivalent to the total emission which would have been produced if the irradiated film had been radioactive, with a specific activity of 1.3 millicuries/mg of CdS. This compares reasonably with the initial specific activities of Rad.-Quartz-1 and 2 which were 1.9 and 1.7 millicuries/mg CdS, respectively.

Adsorption measurements. Electrical conductivity and Seebeck coefficient were measured after exposure of the films to hydrogen, oxygen, and water vapor. Quantitative comparisons of the behavior of radioactive, nonradioactive, and externally irradiated films were made during hydrogen adsorption. Hydrogen was admitted to the films at 40 cm Hg pressure while constant temperature conditions were maintained. Since the films all had an extremely small surface area, no discernible pressure drop took place during adsorption. The change in conductance was used as an indicator of the ionized adsorption of hydrogen. Details of the experimental procedure for hydrogen adsorption measurements are presented by Hearn (9).

RESULTS

In spite of the differences in method of manufacture and grain size, no appreciable differences were observed in the behavior of the Vycor and quartz substrate films.

Temperature Dependence of the Electrical Properties

It was found that the plots of the logarithm of conductance versus the reciprocal absolute temperature obtained during cooling consisted of one or more straight line segments with activation energies ranging

from 0.34 to 0.84 ev. In the temperature range from about 175° to 350°C the activation energies of the various films were generally constant and very similar in magnitude. Typical behavior is shown by the conductance cooling curve plots in Fig. 1 for the films on quartz substrates.

The Seebeck coefficient corresponding to the conductance curves of Fig. 1 is shown in Fig. 2. For all of the films the Seebeck coefficient generally decreased with increasing temperature except for the low-temperature portion of the initial curves of Rad.-Quartz-1 and 2. Furthermore, films with low conductance generally had high Seebeck coefficients, and the Seebeck coef-
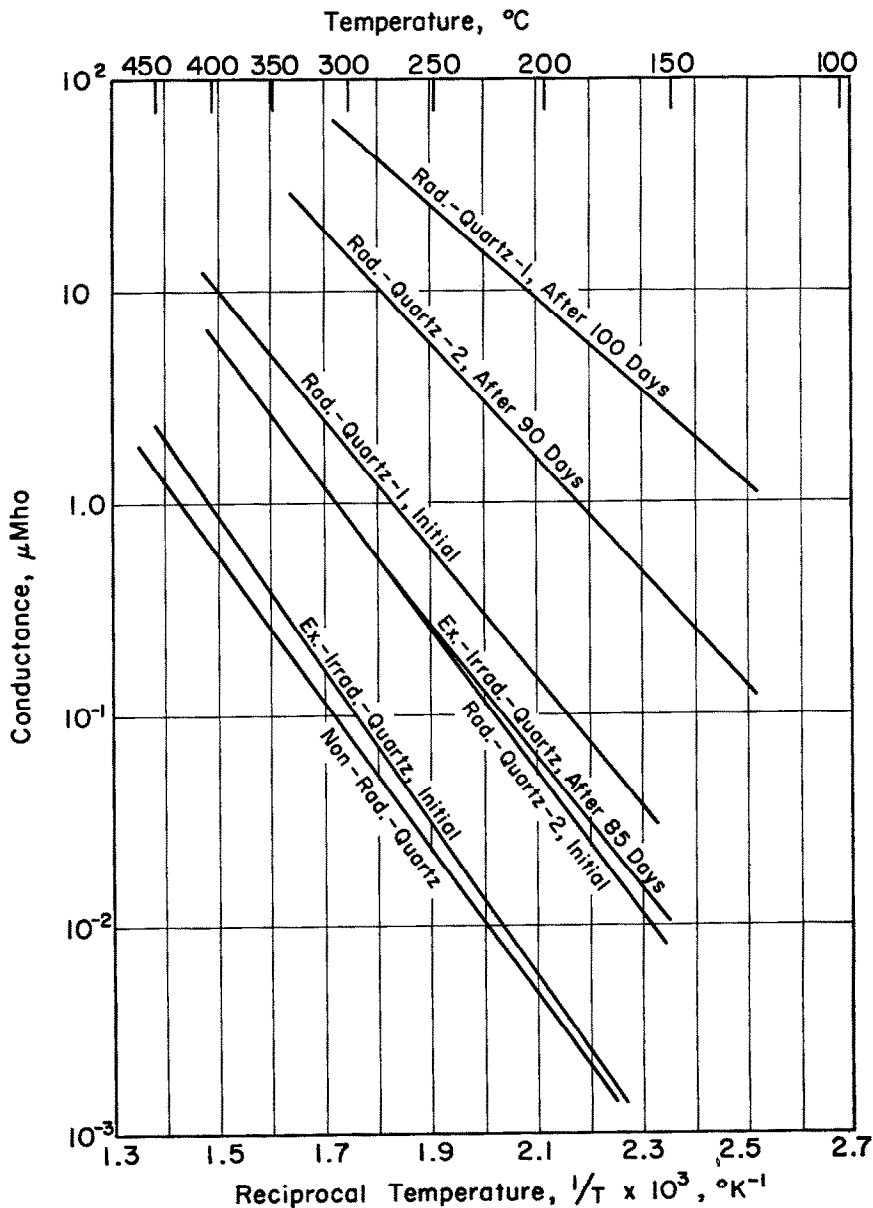

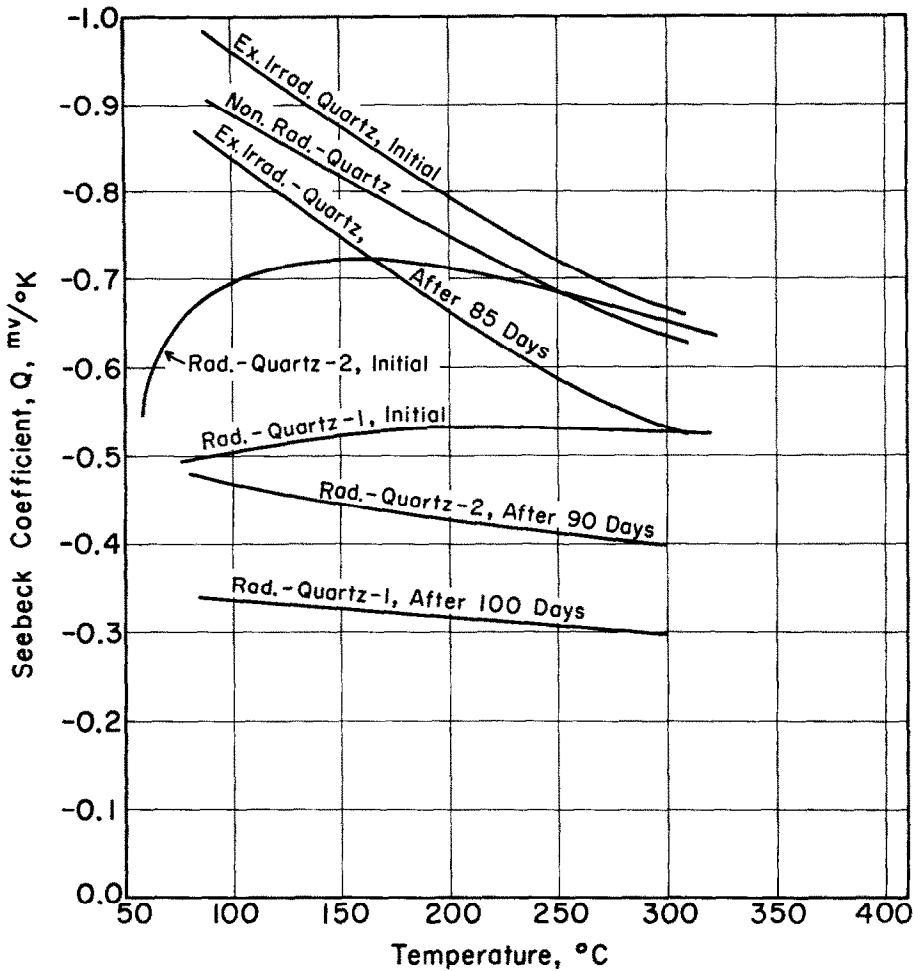FIG. 1. Conductance cooling curves for quartz plate films.

FIG. 2. Seebeck cooling curves for quartz plate films.

ficient of these films decreased more rapidly with increasing temperature than did those of films with high conductances. The sign of the coefficient was always negative, that is, the hot electrode was always positive with respect to the cold electrode, indicating that all the films were n-type as expected (7).

Changes with Time

In radioactive films the decay of sulfur-35 caused the conductance cooling curves to shift upward with time with very little change in slope. This is shown in Fig. 1 by the conductance cooling curves of Rad.-Quartz-1 and 2 after 100 and 90 days,

respectively. A typical conductance increase was two orders of magnitude in 100 days. The conductance of externally irradiated films also increased with time in the same manner but to a smaller extent than that of the radioactive films. An example of this is the film Ex.-Irrad.-Quartz, shown in Fig. 1. Curves for this film show a conductance increase of one order of magnitude after 85 days. In general, such increases in conductance with time were always accompanied by corresponding decreases in the magnitude of the Seebeck coefficient as shown in Fig. 2.

It is noted that the initial values of the conductance of the two radioactive quartz

films are almost an order of magnitude larger than those of the initial curves for the nonradioactive or externally irradiated quartz films. It is believed that this high initial value of conductance is due to the fact that the sulfiding process for the quartz plate films was so long that by the time the first measurement was made, considerable radioactive decay had already occurred. Furthermore, the initial conductance curves for radioactive films with shorter sulfiding times taken immediately after 2–3 days of sulfiding were not appreciably different from those for corresponding nonradioactive films. Thus, the two orders of magnitude conductance increase observed for the radioactive films in Fig. 1 is actually about three orders of magnitude increase above the level of comparable nonradioactive films. Numerical values of the conductance and Seebeck coefficient for several films are listed in Table 1.

Heat Treatment Effects

The electrical properties of all the films are appreciably affected by heat treatment. The response to heat treatment carried out in vacuum is of two types with each type indicating changes in electrical properties in opposite directions. The type of response depends chiefly on the temperature at which the film is held in vacuum. The division between the two response types lies roughly between 400° and 450°C.

The first type, which will be called moderate heat treatment, applies when the heating is kept below 400°C for relatively short periods of time. In general, the radioactive films become noticeably affected by this moderate heat treatment at lower temperatures than the externally irradiated or nonradioactive films. The result of this treatment is a reduction in conductance of all films and an increase in the absolute magnitude of the Seebeck coefficient. This is first observed for the radioactive films at quite low temperatures—below 300°C—in the form of a hysteresis in the conductance measurements at various temperatures. The conductance shows a decrease which depends on the time the film is held at each temperature. With short time intervals at

each temperature the decrease is slight, but when one film, Rad.-Quartz-1, was held at only 115°C for 18 hr the conductance decreased to a final constant value about one-third of its initial value. No similar effects at temperatures as low as this were observed for the nonradioactive or externally irradiated films. The curves shown in Fig. 1 are all cooling curves taken after degassing the films at 300°C and therefore represent a comparison of the films for the same heat treatment. A low-temperature annealing of electrical conductivity in CdS externally irradiated with an electron beam has been reported by Schulze and Kulp (10). Their work, however, was with single crystals.

If this type of moderate heat treatment is carried out on radioactive films at higher temperatures between 300° and 400°C, it is possible to eliminate much of the conductance built up during the radioactive decay. This also applies to the enhanced conductance of externally irradiated films. The corresponding effect for a nonradioactive film is shown by the parallel curves in Fig. 3. Films heat-treated moderately in this manner still furnish stable electrical measurements and, in the radioactive films, subsequent decay will again increase the conductance. This moderate heat treatment does not appreciably alter the slope of the conductance cooling curves but tends to shift the entire curve in the direction of lower conductances.

The second type of response is produced by what is termed severe heat treatment at 450°C or higher for several hours. This causes a large change in the slope of the conductance cooling curves, and, in direct opposition to the results of moderate heat treating, causes a large increase in the magnitude of the conductance. This is shown by the upper curve in Fig. 3. The absolute magnitude of the Seebeck coefficient is lowered drastically and is subsequently unstable with time.

Results of Adsorption Measurements

The adsorption of hydrogen increased the film conductance slightly while oxygen and water vapor greatly decreased the film
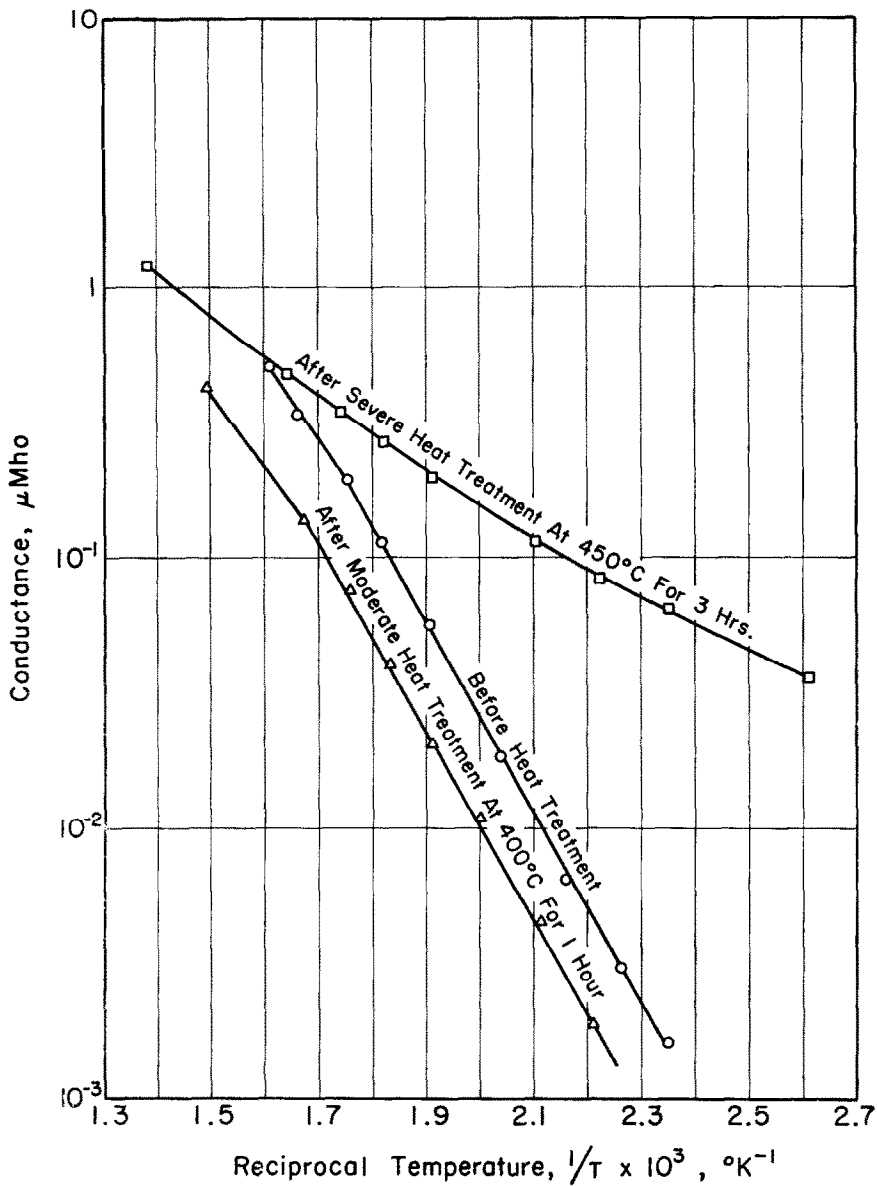
FIG. 3. Conductance cooling curves for nonradioactive film on quartz plate.

conductance. However, the Seebeck coefficient was changed very little by exposure to these gases.

On first admitting hydrogen to the film tubes, an immediate and highly variable jump in the conductance occurred. The magnitude of this sudden increase was not very reproducible. It could have been caused by the abrupt change in the thermal and electrical environment in the tube when hydrogen was suddenly admitted to a high vacuum or it could be a rapid initial adsorption step replaced quickly by a slower mechanism. This initial conductance increase was completed in a few seconds. Following this, the conductance began increasing smoothly and fairly reproducibly over a period of about 40 min. This initial con-

ductance surge has not been considered in the following discussion. Instead the conductance behavior has been studied after an arbitrary starting time taken as 3 min after admitting the hydrogen. As will be shown in the discussion, the amount of ionized adsorption after this time is indicated by the ratio of conductivity at any later time to the conductivity at 3 min. Typical values of the logarithm of this ratio are presented in Table 2 as a measure

DISCUSSION

In the radioactive decay process, the maximum recoil energy which can be imparted to a Cl^{35} nucleus by the ejection of a beta with the maximum energy of 0.167 Mev is about 3.2 ev. The minimum energy which must be imparted to a sulfur atom in the CdS lattice in order to cause a displacement has been reported as 8.7 ev (14). It is likely, therefore, that the Cl^{35}

TABLE 2
VARIATION OF CdS FILM CONDUCTANCE ON EXPOSURE TO H_2 AT 40 CM HG

Film	Age (days)	$\ln \left\{ \frac{c_{40\,min}}{c_{3\,min}} \right\}$	($d \ln c/dt$)			
			$t = 3$ min	$t = 10$ min	$t = 20$ min	$t = 30$ min
			$T = 200°C$			
Non-Rad.-Quartz	—	0.114	6.4	5.0	2.5	2.0
Ex.-Irrad.-Quartz	80	0.113	5.6	4.4	2.8	2.2
Rad.-Quartz-1	15–16	0.107	5.6	4.0	2.25	2.1
Rad.-Quartz-2	100	0.082	4.6	3.6	1.9	1.3
Rad.-Quartz-2	150–155	0.077	3.6	3.0	2.1	1.7
Ex.-Irrad.-Quartz (after moderate heat treatment)	85	—	17.3	15.5	12.1	10.8
			$T = 180°C$			
Non-Rad.-Quartz	—	0.100	7.6	4.7	1.9	1.5
Ex.-Irrad.-Quartz	23	—	3.7	3.4	2.3	2.0
Ex.-Irrad.-Quartz	65	0.095				
Ex.-Irrad.-Quartz	70	0.078				
Ex.-Irrad.-Quartz	79	—	2.7	2.6	2.1	1.7
Rad.-Quartz-2	99	0.056	2.9	2.3	1.2	1.0
Rad.-Quartz-2	152–157	0.048	1.9	1.8	1.2	1.0
Ex.-Irrad.-Quartz (after moderate heat treating)	84	—	6.3	7.0	5.5	4.9
			$T = 150°C$			
Non-Rad.-Quartz	—	0.082	4.4	3.5	2.1	1.3
Ex.-Irrad.-Quartz	22	0.067	2.6	2.5	1.9	1.3
Rad.-Quartz-2	96	0.037	1.1	1.0	0.9	0.9

of the total ionized adsorption between 3 and 40 min after admitting hydrogen at 40 cm Hg pressure. The rate of adsorption at various times is indicated by the time derivative of the logarithm of the conductance. Radioactive decay during the adsorption time is negligible. Table 2 actually presents the average of several repeated measurements on the same type of film.

atoms are introduced into the CdS lattice substitutionally for their S^{35} parents. These chlorine atoms act as donor-type impurities and produce energy levels estimated to be less than 0.05 ev below the conduction band (6, 7), and thus, are essentially all ionized above room temperature. The chlorine concentrations induced are presented in Table 1 and in Fig. 4. The values
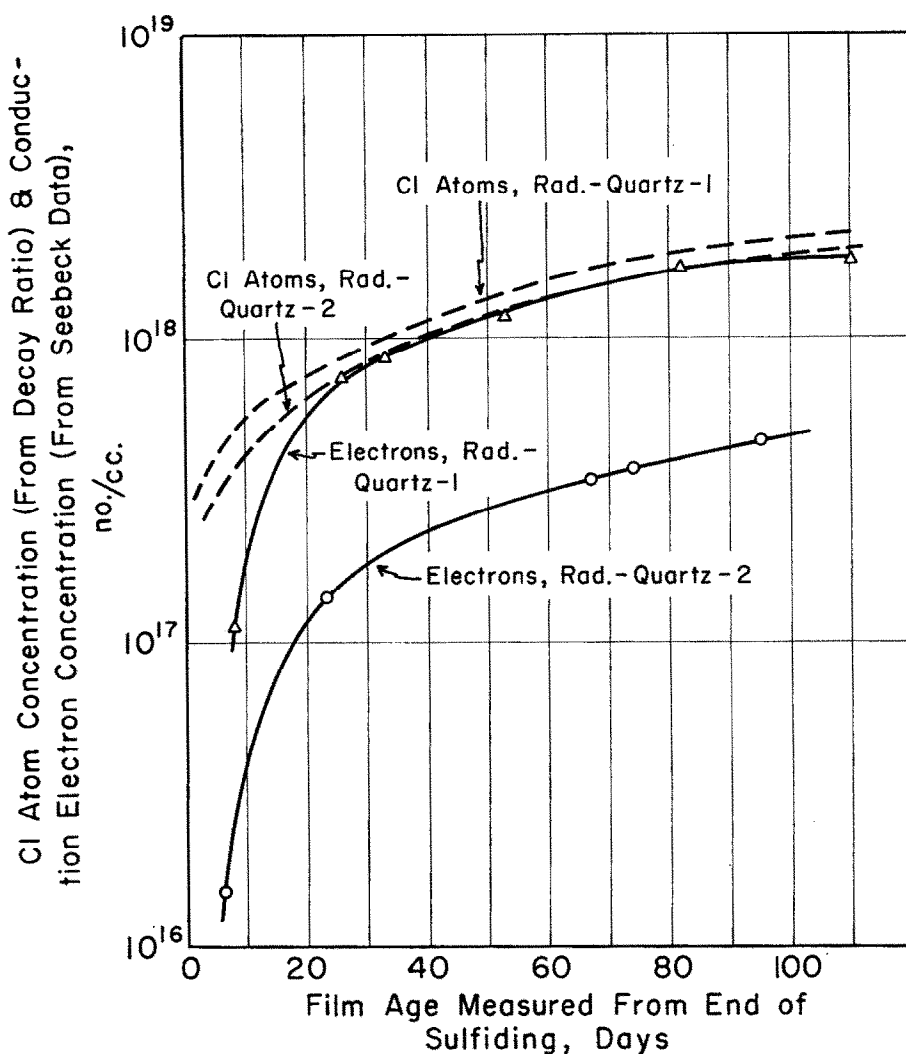
FIG. 4. Increase of apparent conduction electron concentration with time compared to the increase in Cl-35 concentration, for two radioactive films.

of the chlorine concentration at various times were calculated from the known initial S^{35} concentration at the time of film manufacture and the S^{35} half-life. Table 1 and the dashed curves in Fig. 4 show this calculated chlorine concentration. These dashed curves do not show zero concentration of chlorine at time zero because the time scale in Fig. 4 was arbitrarily chosen to begin on the day the H_2S was evacuated from the film. Since the reaction was essentially complete several days earlier, a small

chlorine concentration had already built up by this starting time.

Effects of Polycrystalline Structure

The relation between induced impurities and the concentration of the electrons likely to influence charge-transfer mechanisms is complicated in catalysts because of their polycrystalline nature. Several investigators have proposed a model of polycrystalline semiconductors based on a two-region crystallite. The surface region is charac-

terized by an electrical potential barrier between the crystallites. This barrier controls the conductivity, while the interior region offers much less resistance. Such a model has been proposed by Henisch (12). Assuming that all intercrystallite potential barriers have the same average potential, V, a model similar to that proposed by Henisch predicts

$$c = (Kn) \exp(-eV/kT) \qquad (1)$$

where c is electrical conductivity of the polycrystalline material;

K, a factor which depends chiefly on electron mobility, the intergranular potential barrier, and the film geometry;

n, conduction band electron concentration for the region within the crystallites; and

e, the electronic charge.

The conductances observed here are described very well by this model. The presence of the intergranular barriers is strongly suggested by the effects of adsorbed gases on the electrical properties of the films. Since the observed Seebeck effect was not changed appreciably by adsorbed gases, the observed variation of conductance cannot be explained by variation in bulk current carrier concentration. Thus, the conductance changes during adsorption are logically associated with changes in intergranular potential barriers. This is substantiated by the fact that the slope of the logarithmic conductance cooling curves was changed by gas adsorption, as would be expected from Eq. (1) if V were changed. The postulate of intergranular barrier effects has also been used by Kuwabara (13) to explain the conductance behavior of CdS films exposed to oxygen.

In view of the lack of sensitivity of the Seebeck coefficient to adsorption, the Seebeck coefficient is considered, in terms of this model, to measure properties of the bulk region within the granules while the conductivity results are considered to measure properties of the intergranular barriers. Consequently, the n term in Eq. (1) is indicated by the Seebeck measurements. A cal-

culation of n can only be made using theory applicable to single crystals. However, the use of single crystal results in this application could not be expected to give a valid absolute value for n in the interior of the actual crystallites. The results are useful only to indicate changes in n which occur with the radiation effects. From single crystal semiconductor theory, the Seebeck coefficient, Q, for an n-type material may be related to the Fermi level by

$$Q = [(E_F - E_G)/eT] - Q' \qquad (2)$$

when phonon drag contributions are unimportant (11). In Eq. (2) e is the electronic charge, E_F is the Fermi level, and E_G is the forbidden gap width. Q' is determined by the dependence of the mean free path of the conduction electrons on the electron kinetic energy which, in turn, depends on the operative scattering mechanisms. These scattering mechanisms are not known for the films. However, when E_F is less than E_G, Q' lies approximately between limits shown in Eq. (3)

$$4k/e \geqslant Q' \geqslant 2k/e \qquad (3)$$

where k is the Boltzmann constant.

From the Seebeck measurements of Q and by use of Eq. (2) a range can be found for E_F determined by the limits of Q'. From the limits of E_F a range for n, the apparent conduction electron concentration, can be calculated from Eq. (4):

$$n = \left(\frac{1}{2\pi^2}\right) \left(\frac{8\pi^2 m^*}{h}\right)^{3/2}$$
$$\int_{E_G}^{\infty} \frac{(E - E_F)^{1/2} dE}{\exp(E - E_F)/kT + 1} \qquad (4)$$

When $(E_G - E_F)/kT$ is greater than about 2, which is true for most of the films, Eq. (4) can be closely approximated by:

$$n = n_0 \exp[-(E_G - E_F)/kT] \qquad (5)$$

where $n_0 = 2(2\pi m^* kT/h^2)^{3/2}$. In Eqs. (4) and (5) h is Planck's constant and m^* is the effective mass of a conduction electron. The value of m^* was assumed to be 0.3 times the rest mass of the electron as indicated by the work of Kroger, Vink, and Volger (6) for CdS.

Assuming electronic equilibrium in all parts of the solid, the value of n as obtained from Eq. (5) is thus an indication of the Fermi level. Changes in the value of n indicate changes in the Fermi level throughout the solid. It is only in this regard that these n values are significant. Consequently, they are labeled as "apparent" conduction band electrons for the bulk interior of the granules. In view of the closeness of the Cl levels to the conduction band it is interesting to compare the increase in this apparent conduction electron concentration with the Cl impurity increment brought about by the decay. This is done in Table 1 and in Fig. 4. The solid curves in Fig. 4 are the values of n as a function of time. In view of the exponential form of Eq. (5), changes in n plotted on the logarithmic ordinate in Fig. 4 are directly proportional to changes in the Fermi level.

The deviation of the films from true single crystal behavior is readily apparent in that the value of n obtained from Seebeck data does not increase with temperature in any way comparable to the conductance. In the high conductance radioactive films, n increases only by a factor of from 2 to 3 in the temperature range 400–550°K while the conductance increases from one to two orders of magnitude. The validity of Eq. (1) is also supported by the fact that a change in n caused by impurity doping with Cl should shift the logarithmic conductance cooling curve parallel to itself without appreciable change in slope. This is the observed behavior for the radioactive films, as shown in Fig. 1.

Effects of Cl Impurities

Table 1 gives values of this apparent conduction electron concentration obtained from Seebeck data for several films using both $Q' = 2k/e$ and $4k/e$. The values of n for Rad.-Quartz-1 and 2 at 500°K are plotted in Fig. 4 to compare with the Cl[35] concentration. These n values were calculated using $Q' = 2k/e$ and it is seen that the shape of the n curve in Fig. 4 corresponds closely to that of the Cl[35] concentration, especially for larger values of time. In view of the closeness of the Cl impurity

levels to the conduction band, if the sample were a true single crystal with no traps one would expect the value of n from Seebeck data to be identical to the Cl[35] concentration. For the polycrystalline films, values of the apparent n for Rad.-Quartz-2 were lower than the Cl[35] concentration, although the curves may be brought into virtual agreement by assuming $Q' = 3k/e$ for this film. During the first 30 days or so, the curve for n lies well below the curve for the Cl concentration and is definitely not parallel with it. This could be indicative of initial trapping of electrons donated by the Cl[35]. After several days, sufficient electrons are supplied by the Cl[35] to begin to fill the traps and n increases rapidly. The electrons from the Cl levels finally attain an equilibrium with electrons in all other states and the apparent conduction electron concentration then increases at a rate proportional to that of the Cl[35] increase.

Comparison of Externally Irradiated with Radioactive Films

The differences in behavior of the radioactive films from those externally irradiated with an approximately comparable beta flux indicates the effects of the induced Cl impurities in the radioactive films. These differences are summarized as follows:

(1) A much larger conductance increase occurred with the radioactive films, as shown in Fig. 1. Furthermore, the conductance increase began much sooner in the radioactive films, as shown in Table 1. The results at 500°K are typical.

Film	Conductance at 500°K (μMho)
Non-Rad.-Quartz	0.010
Ex.-Irrad.-Quartz	
7 days	0.023
91 days	0.13
Rad.-Quartz-2	
8 days	0.13
95 days	3.0

(2) The apparent conduction electron concentration, n, calculated from the Seebeck coefficient by Eq. (2) and (5) builds up to a much higher value in the radioac-

tive films than in the externally irradiated ones. Results at 500°K illustrate this.

Film	Apparent n value (no./cc)
Ex.-Irrad.-Quartz	
7 days	0.010
91 days	0.052
Rad.-Quartz-2	
8 days	0.015
95 days	0.46

This indicates a much larger increase in Fermi level for the radioactive film.

(3) The shape of the Seebeck coefficient cooling curves below 300°C is completely different for the two cases, as shown in Fig. 2. The Seebeck coefficient for the radioactive films is less sensitive to temperature than that of the externally irradiated or nonradioactive films.

(4) Removal of the radiation-induced changes by heat treatment begins at a lower temperature in the radioactive films than in the externally irradiated ones.

Since the beta radiation fluxes are nearly alike in the radioactive and externally irradiated cases, the Cl^{35} doping in the radioactive films is the only factor which can reasonably account for the magnitude of the differences. The differences, however, are in magnitude only and not in character.

The first three differences are logical consequences of the elevation of the Fermi level by the introduction of donor impurities in an n-type semiconductor. They are consistent with the polycrystalline model described here by Eqs. (1) and (5) and would be expected if the value of n within the interior of the granules is increased by electrons donated by the chlorine impurities. In the third item, the relative insensitivity of the Seebeck coefficient to temperature for the radioactive films below 300°C is reasonable if the apparent conduction electron concentration in the interior region is controlled by donor impurities with electronic levels very close to the conduction band. At the temperature of this investigation these levels should be completely ionized, producing a relatively large n which undergoes a relatively small percentage variation with temperature. Differentiation of Eqs. (2) and (5) shows that:

$$\frac{1}{n}\frac{dn}{dT} = \frac{e}{k}\frac{dQ}{dT} \qquad (6)$$

After the Cl impurities are ionized at room temperature, any other donor levels available to be ionized by increasing temperature should be the same in the radioactive and externally irradiated films. Consequently dn/dT should be similar in both cases and the radioactive film with the larger n should have the smaller dQ/dT on the right side of Eq. (6).

The behavior of the externally irradiated films is qualitatively similar to the results observed for single crystals of CdS irradiated with monoenergetic electrons in the energy range of 25–150 kev by Schulze and Kulp (10) and by Kulp and Kelley (14). However, these authors found a very high value for the number of conduction electrons added per electron striking the single crystal. They estimated that the number could be as high as six. For the polycrystalline films irradiated here, no comparable number was observed. The maximum number of the apparent conduction electrons produced per incident beta in the Ex.-Irrad.-Quartz film was estimated from Seebeck measurements to be about 0.1 over the first few days of irradiation and only 0.03 over a period of 55 days of irradiation.

Furthermore, Schulze and Kulp found that the effects of irradiation could be easily annealed out by heat treatment at 200°C and that considerable annealing occurred at temperatures well below 200°C. The externally irradiated films studied here showed no appreciable annealing of irradiation effects until they were heated to temperatures in excess of 300°C. These differences in behavior between the irradiated films and irradiated single crystals indicate considerable difference in the nature of the damage. This may be due to the polycrystalline nature of the films or to the fact that the S^{35} beta radiation is not monoenergetic.

However, as indicated in the fourth item of the summary, the radioactive films did

show a low-temperature annealing behavior at temperatures comparable to the data of Schulze and Kulp. In fact, in old radioactive films a large part of the conductance which had been built up on standing for a long time at room temperature was annealed out during the heating to 300°C which necessarily preceded all Seebeck and conductance cooling curve measurements.

This reversal of doping effects by such moderate heat treating is possibly caused by evaporation of Cl impurities or excess Cd atoms. Evaporation of Cl impurities from single crystals of CdS has been reported (7), although at a much higher temperature than 300°C. However, phenomena such as evaporation can occur to a significant extent in thin films at considerably lower temperatures than for bulk materials. For example, CdS films kept at 400°C for several days evaporated to a noticeable extent and visible deposits of CdS condensed in the cooler parts of the vacuum system. If the CdS itself can evaporate, so could Cl impurities or excess Cd atoms. Wendland (16) also observed a large decrease in the conductivity of CdS films upon heating in vacuum above 350°C. The greater sensitivity of the radioactive films to moderate heat treatment in comparison to the nonradioactive or externally irradiated films also suggests the possibility of Cl evaporation to explain the difference. Further work would be needed to definitely prove this, however. The thermal annealing of unknown defects or diffusion of other impurities could be enhanced by the decay process.

Effects of Severe Heat Treatment

The more severe heat treatment at 450°C for several hours drastically reduced the Seebeck coefficient, increased the conductance, and flattened the slope of the conductance cooling curve for many films. This drastic heat treatment probably changes the structure of the film, since after this treatment the Seebeck coefficient was found to be altered by adsorbed gases, indicating a new sensitivity to surface conditions which was absent prior to heat treatment. In terms of the barrier potential model, the flattening of the conductance cooling curve means that this severe heat treatment greatly reduces the intergranular potential in Eq. (1). This apparently does not occur to any appreciable extent with the moderate heat treatment. Furthermore, after the severe heat treatment the electrical properties often changed rapidly with time at low temperatures, indicating an unstable condition. In general, the effects of this type of heat treatment were complicated and no definite suggestions can be made as to the mechanisms involved.

Comparison of Adsorption Rates

Since the Seebeck data show that the adsorption does not change n, but, as shown by the conductivity data, it does change the slope of $\ln c$ vs. $1/T$. Consequently the principle effect of the H_2 adsorption in terms of the model is the modification of the barrier potential, V, in Eq. (1). However, the actual relationship between ionized adsorption and V is very complex. It is simpler to define an empirical relationship between conductance and the amount of ionized adsorption as

$$c/c_I = 1 + K(\Delta N_i) \qquad (7)$$

where c_I is a fixed initial conductance. At a later time, when the conductance is c, the term ΔN_i is the amount of ionized adsorption in excess of that initially present. The justification for this relation is that its differential with time for a fixed initial state conforms to the Elovich equation, which is known to correlate empirically a wide variety of chemisorption rates. The differential of Eq. (7) can be placed in the form of the Elovich equation:

$$dN_i/dt = ae^{-\alpha N}i \qquad (8)$$

where a and α are constants for a given adsorber at a constant temperature. N_i represents the total ionized adsorption at time t. Solving Eq. (7) for N_i gives

$$N_i = [(c/c_I) - 1](1/K) + (N_i)_I \qquad (9)$$

When c_I and N_I are constants, substitution in Eq. (8) gives:

$$dc/dt = Ae^{-Bc} \qquad (10)$$

where A and B are constants. This is then a conductance form of the Elovich Equation which has the integral:

$$c - c_I = (1/B) \ln (t + t_0) - (1/B) \ln t_0 \tag{11}$$

If Eq. (7) is correct and if the Elovich equation represents the rate of ionized H_2 adsorption on CdS, then a time t_0 can be found which will linearize a plot of c vs. ln $(t + t_0)$. This is found to be the case, as shown by the typical result in Fig. 5. Val-

(1) with respect to time, assuming that the ionized adsorption varies only V and in a linear manner. Table 2 presents values of ln (c/c_I) between $t = 3$ min and $t = 40$ min to indicate the total ionized adsorption during this time interval, and also $d(\ln c)/dt$ which measures the instantaneous rates at various times.

Because the constant K in Eq. (12) is unknown, only the comparison of these values is significant. Furthermore, in this comparison it must be assumed that differ-
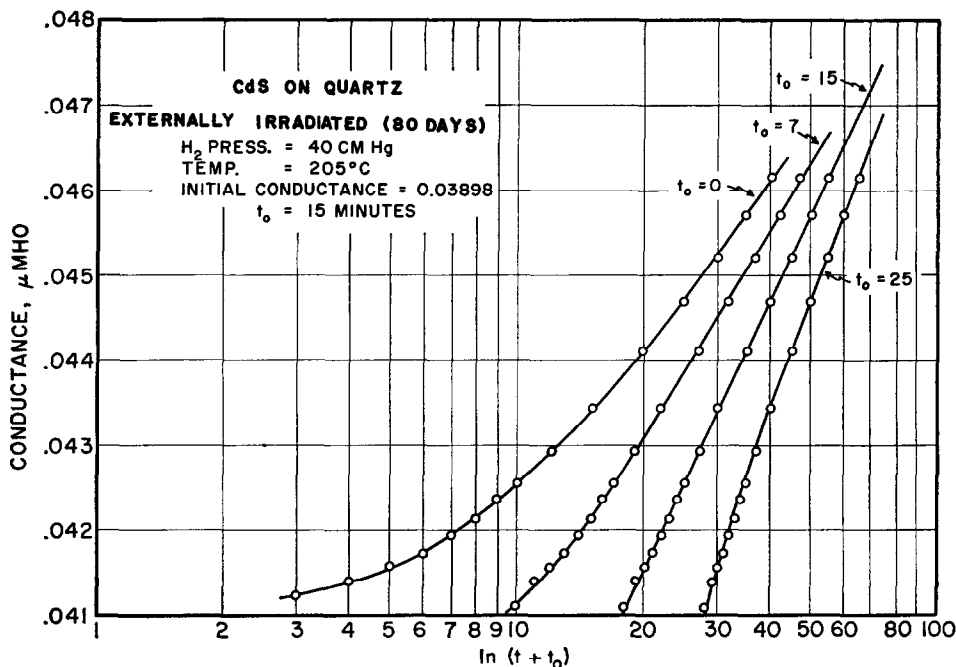

FIG. 5. Increase of conductance on hydrogen adsorption, plotted according to Elovich equation.

ues of t_0 varied between 7 and 15 min for different films.

If the initial conductance c_I in Eq. (7) is considered as a variable the left side of Eq. (7) becomes $(1 + \Delta c/c)$. Then when ΔN_i and Δc are infinitesimally small, the variation with time becomes

$$d \ln c/dt = K(dN_i/dt) \tag{12}$$

showing that the rate of change of ln c at any time is proportional to the instantaneous rate of ionized adsorption at that time. Hearn (9) has shown that this same relation can be derived by differentiating Eq.

ent films with the same method of manufacture have the same adsorption behavior. The quartz plate films were used for this study because they were made under as closely similar conditions as possible. Adsorption results on similar films showed some scatter, particularly at 200°C. The data in Table 2 are actually the average of several determinations. Individual comparisons would occasionally show unexplained anomalies due perhaps to temperature control, film differences, or experimental error in measuring small quantities. The average results, however, generally

show that the total adsorption and the adsorption rate of ionized H_2 decrease with increasing Fermi level. A few points in Table 2 are out of line, particularly where very small quantities are to be compared. The relative position of the Fermi level among the films is indicated by comparing the value of n as given in Table 1. The increase in rate following mild heat treatment of the externally irradiated films is consistent with observed decrease in Fermi level accompanying this process.

These results are similar to those of others who have measured H_2 chemisorption on n-type semiconductors. For example, Cimino, Molinari, and Cipollini (17) have measured H_2 adsorption on ZnO and found a similar relation to the Fermi level when it was varied by adding lithium. The adsorption results are consistent with the results of the electrical measurements in that as the radioactive decay process is most effective in raising the Fermi level; it results in the lowest rate of ionized adsorption of H_2.

CONCLUSIONS

The results of this work have generally established the validity of the technique of doping with the transmutation products of a radioactive decay. These results are summarized as follows:

In the case of a semiconductor such as CdS doped with S^{35}, where the emitted radiation is of low energy, a greater increase in Fermi level is produced by the decay product doping than by the radiation itself. Both effects, however, increase the Fermi level.

This increase in Fermi level in an n-type material results in a proportionate decrease in ionized adsorption for a gas which adsorbs by donating electrons, regardless of how the Fermi level is raised. This was shown to be the case for the ionized hydrogen adsorption studied here.

The electrical properties measured on polycrystalline films can be interpreted consistently in terms of the barrier potential model, in which conductance measurements indicate chiefly the properties of the intergranular barriers, while the Seebeck coefficient indicates chiefly the properties of the bulk material within the granules.

In polycrystalline n-type materials, one cannot always conclude that the increase in Fermi level, or apparent conduction electron concentration obtained from the Seebeck coefficient, will increase in proportion to the donor impurity introduced. In the case of the CdS studied here, this proportionality is attained only after a certain critical Cl impurity concentration is attained.

The increase in Fermi level caused by both impurity doping and externally irradiation can be partially removed by moderate heat treatment. The combination of heat treating and radiation effects, whether external or internal, offers a means of adjusting the Fermi level in a predictable manner to almost any desired level in the same catalytic or chemisorbing material. This offers the interesting possibility of a convenient control over the Fermi level.

Further work will be needed to definitely establish the generality of these conclusions for materials other than the CdS films studied here.

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