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Epitaxial growth of cadmium sulphide on (111) germanium substrates

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Single-crystal expitaxial layers of CdS on (1 1 1) Ge substrates, 8 to 60 μm thick, have been grown from the vapour phase in a closed-tube system. Hydrogen was used as a transport agent. The experimental conditions (source and deposit temperatures, and initial pressure of hydrogen) have been defined where the growth of single-crystal expitaxial layers is feasible. Observations on the morphology of the layers are reported, which suggest that at least two different growth mechanisms should be active in the system. Finally, the composition of the gaseous phase was calculated by assuming a non-reactivity of the Ge substrate with the vapour phase.

1. Introduction

Heterojunctions between cadmium or zinc chalcogenides and germanium or silicon are of great potential value in many fields of applied physics, such as those regarding solar cells [1–4], infra-red detectors (image convertert) [5, 6], heterojunction diodes [7] and triodes [8]. Because of the piezoelectric properties, applications are also suggested for acoustoelectric devices.

The techniques used for growing II-VI compound layers on germanium or silicon are generally physical vapour deposition (PVD) methods [1, 10], although a number of methods are also described which are based on chemical vapour deposition (CVD) (chemical transport [11, 12] and forced-convection sublimation [13]).

In general it is simpler to produce single-crystal layers by CVD rather than by PVD because of a better control on the supersaturation. Also, it is easier to dope the growing layers. On the other hand, the problems of purity and of undesired chemical reactions at the interface introduce severe limitations for a full application of CVD grown heterojunctions. In this paper we refer to the growth of epitaxial layers of CdS on the (1 1 1) planes of germanium, where a vapour-phase chemical-transport reaction is employed in a closed-tube system. To the best of our knowledge, up to now no closed-tube version has been described for the preparation of CdS–Ge heterojunctions; only PVD methods [2, 3, 7, 10] and a vapour-phase chemical-transport method in open-tube version, in one case [11], have been described.

2. Outline of the deposition method

The heterogeneous chemical reaction employed for transporting CdS through a vapour phase is essentially:

$$\mathrm{CdS(s)} + \mathrm{H_2(g)} = \mathrm{Cd(g)} + \mathrm{H_2S(g)}. \qquad (1)$$

The use of hydrogen as a transport agent for Cd and Zn sulphides has already been described [11, 14–18]. In reality Equation 1 is to be seen only as the most important reaction of an associated process where reactions such as

$$\mathrm{H_2S(g)} = \mathrm{H_2(g)} + 0.5\ \mathrm{S_2(g)} \qquad (2)$$

and reactions between solid Ge and H_2S (or S_2) can occur [19]. As will be seen in Section 4, the dissociation of H_2S according to Equation 2 can practically be ruled out and the amount of etching of Ge is not of such an entity as to modify appreciably a transport process governed by Equation 1.

Very simple experimental equipment is employed. It consists of a quartz ampoule 18 to 20 cm long, and 1 cm i.d., divided in two parts by a mid-length narrowing as shown in Fig. 1. The loading of the ampoule is carried out according to

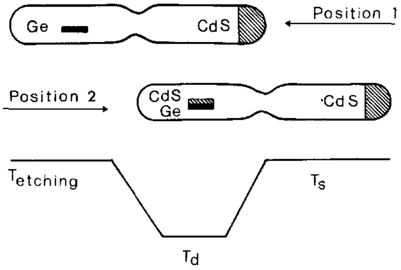

Figure 1 Positioning of the ampoule with respect to the temperature profile. The temperature profile is schematic.

the following procedure: a 99.999% pure CdS powder (purchased from Koch Light Ltd, England) was used as a CdS source. The powder was previously fired at about 800° C in a stream of 15% H_2 in Ar; such treatment is required to eliminate residual volatile impurities, and to increase the grain size of the powder with a partial sinterization in order to avoid a possible suction of the finest grains of the powder during vacuum operations.

The substrates, in the shape of square platelets (about 8 mm x 8 mm x 1 mm) are cut from single-crystal ingots of Ge (purchased from Hoboken, Belgium) and so oriented to have (1 1 1) planes as the largest faces. In this manner the particular mismatch between the (1 1 1)-plane of Ge and the (0 0 1) plane of CdS is reduced to about 2.5%. The Ge surfaces are then lapped with abrasive powders (minimum diameter: Hyprez Diamond Compound I-W-45) and etched with one of the following etching solutions:

(a) 5:1 (volume) – conc. HNO_3 : 37% HF
(b) 1:1:2 – 37% HF : conc. HNO_3 : CH3COOH, plus 100 mg of I_2 per 100 cm^3 solution
(c) 1:1:4 – H_2O_2 : 37% HF : H_20.

After etching, the platelets of Ge are boiled in trichloroethylene, then rinsed with acetone and finally with deionized bidistilled water.

After having introduced about 1 g sinterized CdS powder at one end of the ampoule, and the substrate of Ge approximately at the centre of the other half of the ampoule (as indicated in Fig. 1), the ampoule is connected to a vacuum line and kept under a vacuum greater than 10^{-5} Torr for about 2 h. Then the required initial pressure of hydrogen ($P^0_{H_2}$) is introduced through a needle valve. Dried hydrogen is obtained by passing the gas stream through liquid-nigrogen traps. The ampoule is then closed and placed in a tubular furnace, i.d. 2 cm; the temperature profile of the furnace is schematically shown in Fig. 1. Temperature profiles of this shape, with a minimum temperature, have already been used [20]. They are easily obtained with two separate Kanthal heating elements, each individually controlled.

TABLE I Layer thickness at different experimental growth conditions

T_s:T_d (°C)	P_{tot} (atm)	Deposition time (h)	Thickness (μm)
730:650	1.0	20	8
730:650	1.2	40	38
760:660	1.2	65	57
760:680	1.3	94	62

The ampoule is initially placed in position 1 of the figure, in order to have a thermal etching of the substrate surface, then it is pulled into position 2, where the deposition of CdS begins to form on the substrate positioned in the minimum temperature of the profile.

3. Results

The best results are obtained when the source temperature (T_s) is between 730 and 760° C, the deposition temperature (T_d) between 630 and 680° C, and $P^0_{H_2}$ between 200 and 300 Torr at room temperature. In the above range of temperatures, with $P^0_{H_2}$ lower than 200 Torr, no complete epitaxial layer was observed, even for long deposition times (90 h; average deposition times are 40 to 60 h), although the deposition zone was completely covered by transported CdS. Values of $P^0_{H_2}$ higher than 300 Torr have not been tested.

The epitaxial deposition generally appears as a smooth transparent yellow layer of CdS, which proves to be a single crystal at all the points where a Laue-diagram has been taken. The thickness of the layers changes with the varying of the experi-

Figure 2 Chemical-etching figures on the outer face (Cd face) of a CdS layer. Etching solution: 37% HCl, ×300.

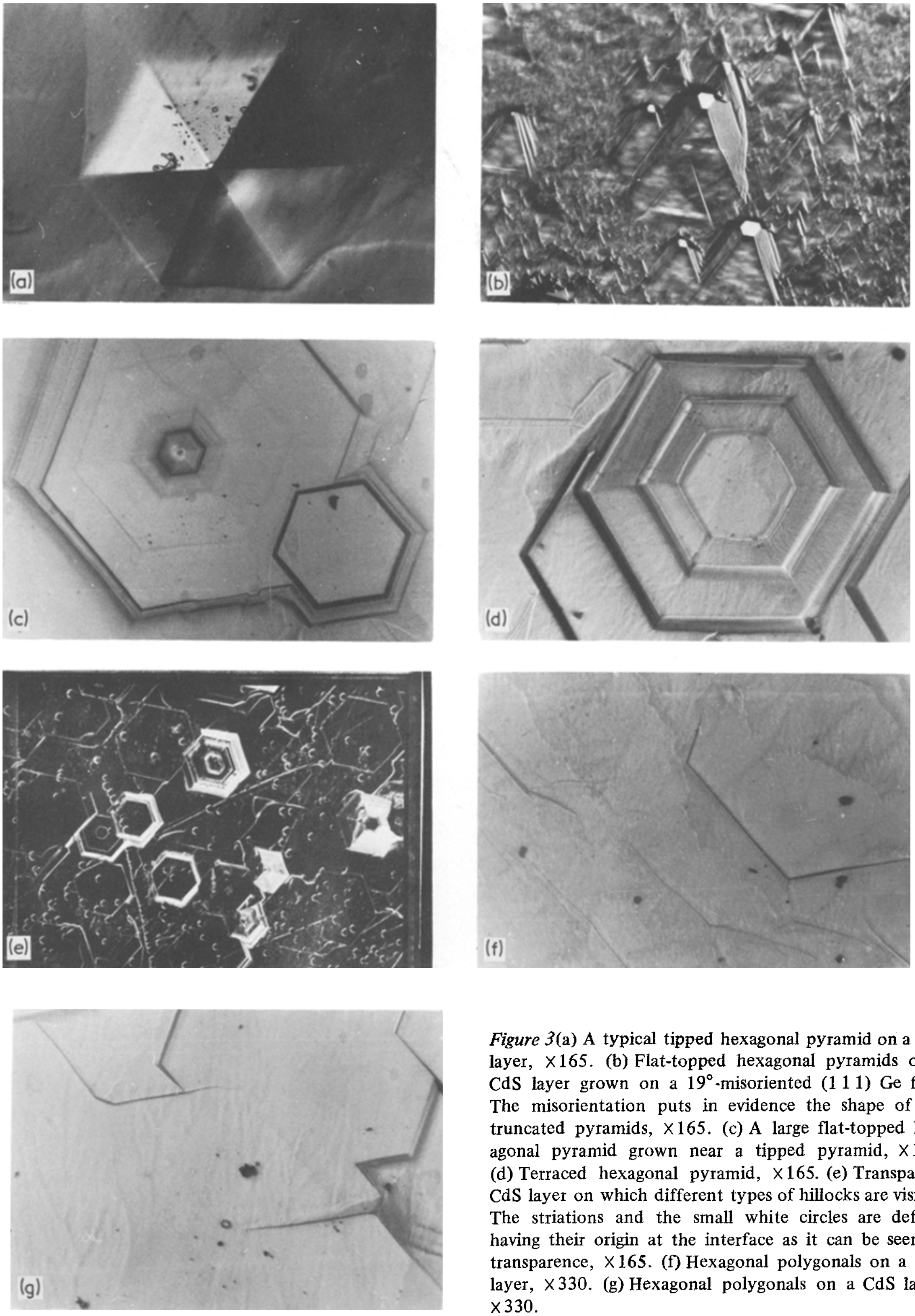

Figure 3(a) A typical tipped hexagonal pyramid on a CdS layer, X165. (b) Flat-topped hexagonal pyramids on a CdS layer grown on a 19°-misoriented (1 1 1) Ge face. The misorientation puts in evidence the shape of the truncated pyramids, X165. (c) A large flat-topped hexagonal pyramid grown near a tipped pyramid, X165. (d) Terraced hexagonal pyramid, X165. (e) Transparent CdS layer on which different types of hillocks are visible. The striations and the small white circles are defects having their origin at the interface as it can be seen by transparence, X165. (f) Hexagonal polygonals on a CdS layer, X330. (g) Hexagonal polygonals on a CdS layer, X330.

mental conditions. Although a systematic investigation of variation in thickness with experimental conditions was not performed, some typical values can be represented by those reported in Table I, obtained by cutting the layer parallel to the [1 1 1] axis of Ge and then measuring the layer thickness on a microphotograph.

From chemical-etching patterns [21] it was possible to ascertain that the layer face adjacent to the (1 1 1) Ge face was an S face. This crystallographic relation is in agreement with that observed by Dijk and Goorissen [11], but in contrast to that observed at lower temperatures, when PVD methods were employed for growing the CdS-layers [10].

A Cd face etching pattern of the outer CdS face is shown in Fig. 2.

3.1. Morphology of the deposition

The morphology, as observed by optical microscopy, varies with some regularity with variation in $P^0_{H_2}$ and T_d, although it seems rather insensitive to T_s variations and to the type of chemical etching pretreatment of the substrate.

In general, at lower T_d (about 630 to 650° C) a texture appears which consists mainly of hillocks in the shape of either well-tipped or truncated (flat-topped) pyramids. The truncated-to-tipped pyramid density ratio increases with $P^0_{H_2}$, while the height-to-base-area ratio decreases. At higher $P^0_{H_2}$, tipped pyramids tend to disappear and the truncated pyramids are gradually transformed into hexagonal prisms with a very low height-to-base-area ratio. Similar structures have already been described in the expitaxial deposition of CdS [16]. At still higher $P^0_{H_2}$ (about 260 to 280 Torr), few incomplete hexagonal polygonals predominate on highly perfect smooth layers. Fig. 3 illustrates these structures. These morphologies seem to originate from a lateral-step-motion mechanism: in the presence of impurities screw dislocations originate which give rise to the formation of the observed hillocks. In this respect a suggestion is given by the observation in some cases of hexagonal growth spirals (Fig. 4).

At higher T_d (650 to 680° C), when $P^0_{H_2}$ is in the range of 260 to 280 Torr, the shape of the hillocks becomes rounded and takes on the typical "mesa" or "plateau" structure previously described [22]. An example is given in Fig. 5. The density of such rounded structures decreases as $P^0_{H_2}$ increases and the perfection of the layer markedly improves. It has been suggested [22] that such "mesa" structures are probably due to a lateral bulk diffusion mechanism which overlaps the former lateral-step-motion mechanism.

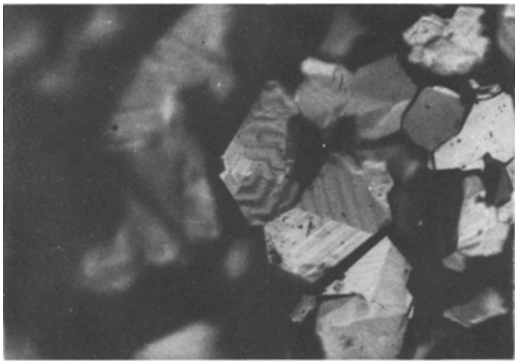

Figure 4 Hexagonal growth spirals on a polycrystalline layer, × 165.

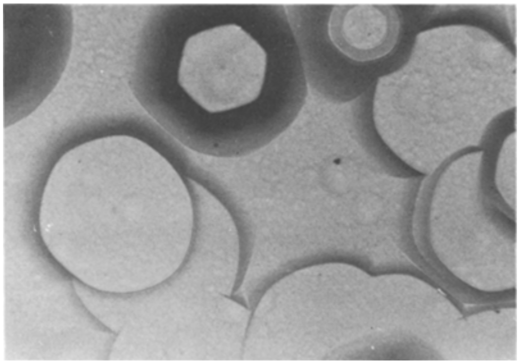

Figure 5 Typical "mesa" or "plateau" structures on a CdS layer, × 165.

At still higher T_d (> 680° C), there is a tendency for the layer to become polycrystalline: the hillocks assume irregular rounded shapes and the degree of coalescence becomes poorer (Fig. 6). In some cases the hillocks end in irregular hollow structures (Fig. 7). Polycrystalline layers are also

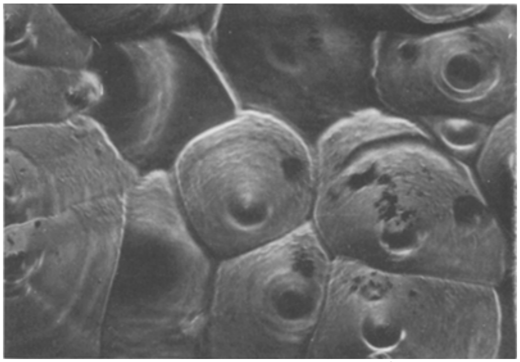

Figure 6 Rounded irregular hillocks in a layer grown at high deposition temperature. The degree of coalescence between the hillocks is poor, × 165.

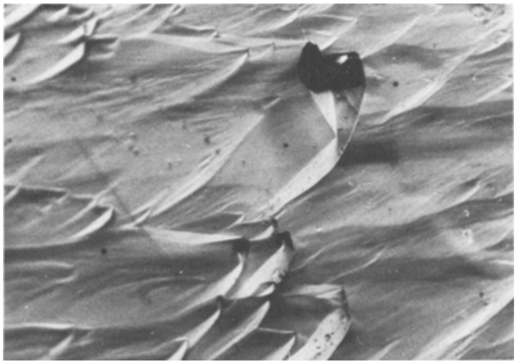

Figure 7 Irregular texture on a CdS layer where hollow structures are observable. The deposition temperature was higher than 680° C, × 165.

generally obtained when the substrates are not well positioned in the minimum temperature profile. In this case a certain degree of dissolution of the substrate and a certain amount of a black deposit on the quartz wall of the ampoule are observed.

3.2. Electrical properties of the junction

Some preliminary electrical measurements have been performed on some n-CdS/Ge-p heterojunctions, and in all cases low rectification coefficients of the order of 3 to 6 at 100 mV of applied voltage have been observed in the current–voltage characteristics. In particular, there appears a marked reverse-current dispersion. Work is presently under way in order to determine the reasons for the heterojunction softening.

4. Chemical transport process in the vapour phase

When epitaxial depositions are carried out in a closed-tube chemical-transport system three problem areas must be taken into account:

(i) the definition of the chemical-transport reactions, implying knowledge of the composition of the gaseous phase;

(ii) the role of the vapour-phase kinetics, i.e. by which fluid-dynamic mechanisms and at which rate the gaseous species are transported from the source zone to the deposition zone;

(iii) the nature of the processes which take place at the layer–substrate interfaces; these processes are generally expected to reduce the growth rate as calculated on the basis of the vapour-phase kinetics.

In our case, (i) does not cause particular difficulties, provided the problem is simplified by assuming a non-reactivity of the Ge substrate with the vapour phase. Also, the fluid dynamics of the vapour phase, point (ii), do not in principle pose great difficulties. Various theoretical approaches are available which enable one to calculate with sufficient accuracy the net flux of CdS through the vapour phase [23–26]. However, a definition of the limiting nature of the condensation process on the vapour-phase kinetics (point iii) is very difficult to give in the present state of knowledge of the surface processes [27, 28]. In the next Section 4.1 we evaluate, on a thermodynamical basis, the compsotion of the vapour phase in terms of partial pressures of the gaseous species.

4.1. Vapour-phase composition

The partial pressures of the gaseous species can be calculated for any pair of overall pressures (P) and temperatures (T) by solving the following set of equations:

$$\sum_i P_i = P \quad \text{(Dalton's law)} \qquad (3)$$

$$\prod_i P_i^{q_{ia}} = K_a \quad \text{(chemical equilibria)} \qquad (4)$$

$$\frac{\sum_i \nu_{i\mathrm{Cd}} P_i}{\sum_i \nu_{i\mathrm{S}} P_i} = (\mathrm{Cd/S}) \qquad (5)$$

where $i = 1, 2, \ldots, 4$ are the gaseous species in the system; $a = 1, 2$ are the chemical reactions; q_{ia} is the reaction coefficient of the ith species in the ath reaction; (Cd/S) gives the atomic Cd-to-S ratio, which has to be conserved; finally $\nu_{i\mathrm{Cd}}$ and $\nu_{i\mathrm{S}}$ are the stoichiometric coefficients of the Cd and S atoms respectively in the ith molecular species. In the absence of any excess Cd or S, we have (Cd/S) = 1.

The numerical values of the equilibrium constants K_a are given by the relationships [29, 30]:

$$\log K_1 = 7.42 - 12089/T$$

$$\log K_2 = 2.58 - 4718/T.$$

The Equations 3 to 5 can easily be solved by numerical methods. In Fig. 8, values of partial pressures of the gaseous species are plotted against T for some values of P, and for (Cd/S) = 1. The S_2(g)-pressure is not reported, since it never exceeds 10^{-5} atm. This means that only Equation 1 is active in the chemical-transport process. Finally, the relationship between the initial H_2-pressure introduced in the system at a given temperature T_0 and the overall pressure P reached by the sys-

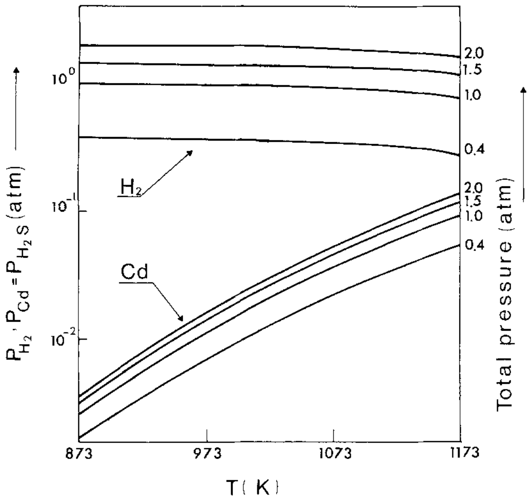

Figure 8 Partial pressures in the CdS:H_2 system against temperature, when (Cd/S) = 1. The total pressure of the system is given for all curves.

tem at the equilibrium temperature T (which can be regarded as the average temperature of the system) is given by:

$$P^0_{H_2} = TT_0^{-1}\,[P_{H_2}(P, T, (Cd/S)) + P_{H_2S}(P, T, (Cd/S))]\,. \qquad (6)$$

In Fig. 9, $P^0_{H_2}$ is reported against P for (Cd/S) = 1 and for some values of T when $T_0 = 300$ K.

5. Conclusion

In this article a very simple closed-tube chemical-transport method has been described by which single-crystal CdS layers can be epitaxially deposited on the (1 1 1) face of Ge substrates. It is shown that some morphological features (differently shaped pyramids and rounded structures) change as the experimental growth conditions are changed, and it is proposed that at least two different mechanisms are responsible for these different growth structures.

Preliminary experiments on the electrical properties of the n-CdS/Ge-p heterojunction indicate a marked softening of the device at room temperature. Finally, the composition of the vapour phase has been calculated, showing that a single heterogeneous reaction is sufficient to describe the chemical-transport mechanism in the vapour phase.

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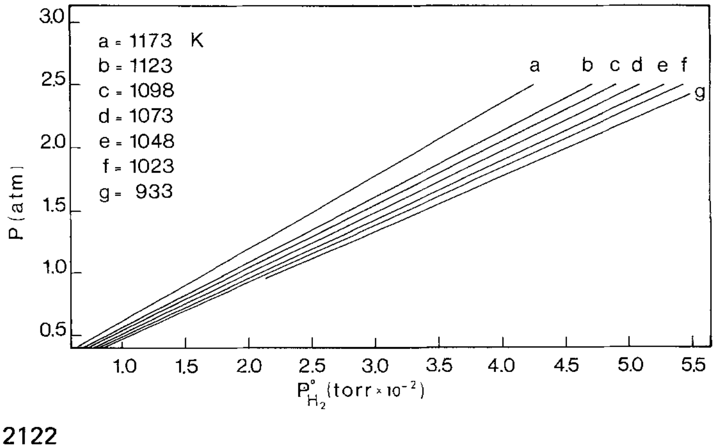

Figure 9 Total pressure in the CdS:H_2 system against the initial pressure of hydrogen, for various average temperatures.

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