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SINGLE CRYSTAL GROWTH OF P–DOPED $CdSiAs_2$†

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ABSTRACT

$CdSiAs_2$ single crystals were grown in a closed tube system by chemical vapor transport using bromine or cadmium chloride as a transport agent. Large planar and prismatic elongated crystals were grown within a small temperature gradient (0.5 to 1 K/cm). The crystals were *p*-type. Crystal doping during the growth could be achieved by employing boron or aluminum as a doping agent. The net carrier density ranged from 4×10^{13} to 8×10^{17} cm^{-3}, and the Hall mobility from 100 to 300 cm^2/V s at room temperature. Photoluminescence spectra showed peaks at 1.600, 1.615, 1.635, 1.789 and 1.855 eV. The lowest band-to-band transition was observed from liquid helium to room temperature. XPS-measurements showed an improved surface stoichiometry of the $CdSiAs_2$ single crystal surface after removal of a Si-rich oxide layer by dilut HF.

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1. Introduction

For several years, ternary semiconductor compounds with the chalcopyrite structure including the II-IV-V_2 compounds have been studied and proposed for device applications [1-4]. $CdSiAs_2$, in particular, as one of the ternary analogs to GaAs, is suitable for solar cell [5,6] and photocathode [7,8] applications. Due to spin-orbit coupling and crystal field splitting, the valence band degeneracy of GaAs is completely lifted in $CdSiAs_2$, and three direct band gaps—with transition energies of 1.55 (A in fig. 6), 1.74 (B) and 1.99 eV (C) at room temperature—can be observed [3]. The lowest direct bandgap A lies in the appropriate range for photovoltaic solar energy conversion. ZnO/$CdSiAs_2$ heterojunction solar cells have been prepared [9]. Excitation with circularly polarized light across the second direct bandgap B is expected to deliver 100% spin-polarized electrons. To produce spin-polarized photoelectrons, a (001)-surface of a highly doped p-type single crystal with negative electron affinity is necessary [7,8].

$CdSiAs_2$ melts incongruently between 821 and 943°C [10], so that crystal pulling from a melt is impossible. This leaves chemical vapor transport (CVT) techniques [11-14] and flux techniques [15,16] as methods for growing $CdSiAs_2$ bulk single crystals. We decided to use the CVT technique because it allows the growth of highly pure crystals with an excellent surface perfection. Here, we describe for the first time the reproducible growth by halogen CVT in a closed tube system of large p-type $CdSiAs_2$ single crystals with low resistivities. The crystals are characterized by Hall-effect measurements, photoluminescence spectroscopy and x-ray photoelectron spectroscopy (XPS).

2. Experimental Details

MATERIAL PREPARATION AND CRYSTAL GROWTH

We proceeded in two steps: synthesis of polycrystalline $CdSiAs_2$ from the constituent elements and crystal growth by CVT, both in sealed quartz ampoules.

The quartz ampoules had been cleaned by etching with a mixture of concentrated HF and HNO_3, followed by thorough rinsing with distilled and then deionized water. All synthesis and crystal growth was carried out in evacuated (10^{-5} Torr) and sealed ampoules.

The polycrystalline starting material was prepared by holding stoichiometric amounts of cadmium, silicon and arsen (purity better than 99.999% for all elements) sealed in a 19 mm diameter quartz ampoule at a temperature of 815°C in a two-zone furnace for two-week periods. In order to localize the material, the furnace was tilted at 5°C and a temperature gradient maintained across the ampoule, thus ensuring that volatile elements were returned to the reaction site. X-ray investigation showed that the prereacted material was $CdSiAs_2$. The polycrystalline $CdSiAs_2$ material synthesized in one ampoule ($\sim$ 10 g) was subsequently used for one single crystal growth run.

The polycrystalline $CdSiAs_2$ material (crushed into 5 mm lumps), the chemical transport agent and the dopant, if any, were placed into a 24 mm diameter quartz ampoule. The transport agents were liquid bromine, or cadmium chloride, or aluminum chloride (the latter are white crystalline powders). The quantity of the liquid bromine was varied between 1.0 and 1.2 $\mu\ell/cm^3$, and of the crystalline chlorides between 1.5 and 3.0 mg/cm^3. The sealed ampoule was placed

at the bottom of a vertical, three-zone furnace for a period of three to six weeks. Figure 1 shows the temperature profile. The starting material was placed in the cooler part of the ampoule at the source temperature, extending a little over two-thirds of the ampoule length. The source material was held between 793°C and 805°C, and the average gradient was kept between 0.5 and 1.0 K/cm. The crystals were doped with either boron or aluminum. The boron was introduced in the starting material as boron-doped (instead of undoped) silicon. The aluminum chloride served as the dopant source for aluminum. The covalent radii of boron (0.82 Å) and aluminum (1.18 Å) are similar to the radius of silicon (1.11 Å). The radii of cadmium (1.48 Å) and arsen (1.20 Å) are larger (all radii from ref. [17]).

MEASUREMENT PROCEDURES

Ohmic contacts were applied to the crystals for electrical measurements. These crystals were etched in a solution of 5 vol% of concentrated HF in water for one minute, and then rinsed with distilled water and with propanol. Gold and silver were evaporated sequentially. Occasionally, poor electrical contacts were improved with a short electric pulse with energies ranging between 0.1 and 10,000 mW s. The voltage, current and time of the above pulse could be varied between 1 and 100 V, 1 and 100 mA, and 100 and 1000 ms, respectively. The conductivity type was determined by thermoprobe and Hall-effect measurements. The electrical conductivity and Hall-effect measurements were carried out between 33 and 400 K on Van der Pauw patterns, and were evaluated with a computer-controlled data acquisition system [14].

The photoluminescence measurements were carried out with a standard setup [18,19], between liquid helium and room temperatures. Argon or krypton lasers were used for excitation. Since the luminosity of the investigated $CdSiAs_2$ surfaces was low, all spectra were taken using an entrance slit width of 300 μm and the first order diffraction of the grating. The resolution over the investigated energy range was better than 1 meV.

The surface analysis was carried out with a computer-controlled XPS apparatus, with a resolution better than 0.5 eV. All peak energies were related to the carbon 1s peak at 285.0 eV. The escape depth of the photoelectrons was about 30 Å. We determined the surface composition by an integration of the XPS peak areas, adjusted for differences in atomic cross sections.

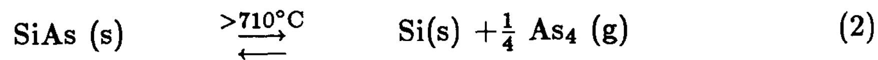
3. Results and Discussion

Crystal Growth and Doping

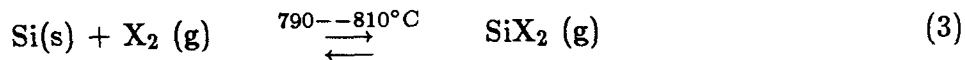
Figure 2 shows that the single crystals grew all along the top of the source material and nearly perpendicular to the ampoule axis. The habit of the single crystals depended on the transport agent. Cadmium chloride produced a prismatic elongated habit. These crystals often were hollow, and their surface appearance was less perfect than the surface of crystals grown with bromine. Bromine-grown crystals were flatter and less hollow (see fig. 3). In both cases, the large crystal surfaces (up to 50 mm^2) belonged to the (112) or (101) from ref. [13]. The crystals were, at most, 15 mm long.

Using our growth data and the decomposition scheme given by Smith and coworkers [10], we suggest the following growth reaction scheme:

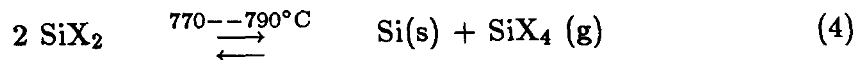
$$\mathrm{CdSiAs_2\ (pc)} \underset{}{\overset{570-710^\circ\mathrm{C}}{\rightleftarrows}} \mathrm{SiAs(s) + Cd(g) + \tfrac{1}{4}\ As_4(g)} \quad (1)$$



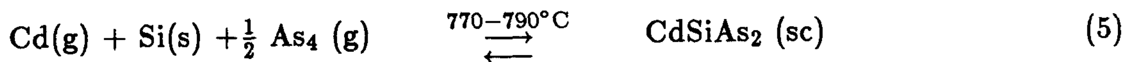
$$\mathrm{SiAs\ (s)} \overset{>710^\circ\mathrm{C}}{\rightleftarrows} \mathrm{Si(s) + \tfrac{1}{4}\ As_4\ (g)} \quad (2)$$



$$\mathrm{Si(s) + X_2\ (g)} \overset{790-810^\circ\mathrm{C}}{\rightleftarrows} \mathrm{SiX_2\ (g)} \quad (3)$$



$$\mathrm{2\ SiX_2} \overset{770-790^\circ\mathrm{C}}{\rightleftarrows} \mathrm{Si(s) + SiX_4\ (g)} \quad (4)$$



$$\mathrm{Cd(g) + Si(s) + \tfrac{1}{2}\ As_4\ (g)} \overset{770-790^\circ\mathrm{C}}{\rightleftarrows} \mathrm{CdSiAs_2\ (sc)} \quad (5)$$

pc = polycrystalline, s = solid, g = gaseous,

X_2 = Cl_2, bromine, sc = single crystalline .

From eqs. (3) and (4), one can easily understand that the use of chlorine as a transport agent led to accelerated growth, due to its higher chemical reactivity. A reduction of the amount of transport agent or of the temperature gradient reduced the growth rate and produced crystals similar to those grown with bromine.

Electrical Transport Properties

All the $CdSiAs_2$ single crystals were p-type. Their resistivities ranged from 0.07 to 10,000 Ωcm at room temperature. The Hall mobility μ_H lay between 100 and 300 cm^2/V s at room temperature. The average value of $d\ln\mu_H/d\ln T$ between ~ 200 K and room temperature is −1.5, indicating that charge carrier scattering at acoustic phonons dominates. The value of the net acceptor density p at room temperature varied between 4×10^{13} and 8×10^{17} cm^{-3}. The temperature dependence of μ_H and p of typical samples is shown in figs. 4(a) and 4(b).

The native acceptor level observed in undoped samples exhibited activation energies E_A between 170 and 300 meV. The aluminum- and boron-doped samples showed values of 9 and 23 meV, respectively. E_A, given by the slope of $\ln p$ as a function of $1/T$, became smaller with increasing p, as can be seen in fig. 4(b).

We extracted values for the acceptor energy in two steps. In the first step, we determined the acceptor ionization energy for each sample separately, assuming partial compensation. In the second step, we used a conventional one-acceptor/one-donor model [20,21] and assumed a complete ionization of the donor level. A one-acceptor/one-donor model does not exclude the existence of other impurity levels, but assumes that one level dominates. The total number of impurities is taken into account by the degree of compensation K, which is defined as $K = N_D/N_A$.

We used a least-square fit procedure (Gauss-Newton) of $\ln p$ to $1/T$. The measured net hole density p was fit to the well-known eq. [22]

$$p \, \frac{p + N_D}{N_A - N_D - p} = \frac{1}{D} \, 2 \, \frac{(2\pi m^* kT)^{3/2}}{h^3} \, \exp\left\{-\frac{E_A}{kT}\right\} ,$$

where N_D is the donor concentration, N_A the acceptor concentration, D the degeneracy factor of the acceptor level, m^* the effective mass of the holes, k the Boltzmann constant and h the Planck Constant. The fit was considered to be sufficiently convergent when the consecutive least-square minima changed less than 10^{-10}. After that iteration step, the procedure was stopped. The calculated activation energies were within $\pm 10\%$ of the values estimated from the slopes of p. From this observation, we conclude that the assumption of carrier

compensation is correct. The calculated compensation degrees K range between 0.02 and 0.47.

E_A depends on the hole concentration. E_A is plotted versus the cube root of p at 300 K in fig. 5. The fitted linear dependence $E_A(p) = E_A(0) - \alpha p^{1/3}$ is in agreement with the theory of Pearson and Bardeen [23], as modified by Debye and Conwell [24]. This theory invokes Coulomb interaction between ionized levels, to explain the decrease in E_A with increasing p. The fit to the data of fig. 5 yields $E_A(0) = 310$ meV and a screening constant $\alpha = 6.7 \times 10^{-4}$ meV cm. We must mention that the boron-doped sample with $E_A = 23$ meV (see fig. 5) also obeys the above law; however, the aluminum-doped (9 meV) does not.

Photoluminescence

A typical photoluminescence spectrum of a $CdSiAs_2$ single crystal obtained at liquid helium temperature, with an excitation power ~ 20 mW and excitation wavelength ~ 570 nm, is shown in fig. 6. We attribute the low-energy peak at 1.600 eV to a Donor-Acceptor-Pair transition (DAP), since its energy shifted towards smaller values with reduced excitation power. The peak E_1 at 1.615 eV showed no dependence on excitation power, a necessary condition for a DAP attribution. The Hall-effect measurements did not show a 20 meV acceptor level and the shape of the photoluminescence peak is not asymmetric, as it should be in the case of a Band-Acceptor-Transition (BAT) [25]. The literature gives contradictory interpretations, either as a BAT [3,11,26,27] or a DAP [28]. We tentatively propose a donor-bound exciton as the origin of this peak at 1.615 eV.

Our proposal is supported by the constant energy shift with respect to transition A over the entire temperature range from liquid helium to 90 K. This can be seen in fig. 7. Our proposal is supported also by the disappearance of the peak at $\sim$ 90 K. The next transition can be clearly attributed to the lowest band-to-band transition A at 1.635 eV. The energy of this transition varies as a function of temperature (see fig. 7), according to the empirical formula [29]

$$E_g = E_0 - \frac{\beta T^2}{T+\gamma} .$$

A fit yields the bandgap energy at 0 K $E_0 = 1.64$ eV and the constants $\beta = 7.84 \times 10^{-4}$ eV/K and $\gamma = 587$ K. The room temperature value of transition A with 1.55 eV agrees with the results of Shay and Wernick [3]. We ascribe the two high-energy transitions at 1.789 eV and 1.855 eV to the second direct bandgap B. Since the intensities of the above peaks were too low to measure as a function of T, we assume here the same temperature dependence as for transition A; then transition B has the value of 1.78 eV at room temperature. This value is in good agreement with the value of 1.74 eV given in ref. [3]. The peak E_2, separated by 66 meV from B could again be due to an exciton. Finally, we observed a small bump above the noise at 2.13 eV. Extrapolating to room temperature, as explained above, we obtain a value of 2.05 eV, which is also in good agreement with the value for the direct transition C of 1.99 eV given in ref. [3]. Therefore, our photoluminescence data confirm the band scheme found by electroreflectance measurements [3].

SURFACE CHEMISTRY

Because of the possible application of $CdSiAs_2$ as a source of spin-polarized electrons, we studied the composition of its surface by XPS. We investigated three different surface conditions:

(1) as-grown single crystal surface stored in air;

(2) condition (1), plus an etch with a solution of 5 vol% of concentrated HF in water for one minute;

(3) condition (2), followed by an ion-etch ($\sim$ 15 monolayers).

Typical spectra for the three conditions are shown in fig. 8.

Condition (1) produced low-intensive peaks of Cd, Si, As and C at the energies summarized in Table 1. A comparison with the reference data [30] and the spectra for surface conditions (2) and (3), shows that the Si and As peaks are shifted by 2 to 3 eV towards higher energies; therefore, condition (1) probably represents an oxidized surface. The entire spectrum (including the carbon peak) was shifted towards higher binding energy. This indicates the existence of a thick, insulating layer at the surface. In summary, condition (1) corresponds to an insulating, oxidized surface layer. Integration of the areas under the peaks yielded a surface stoichiometry ratio of Cd:Si:As = 1.5:15:2. Thus, the surface contains an excess of Si, probably due to evaporation of Cd and As during the cool-down at the end of the growth run. Carbon contamination of the surface is estimated at 23 at%.

In condition (2), all peaks of the spectrum were more intense, and an additional peak at $\sim$ 205 eV, due to As 3s, appeared. The energies of the Si and As peaks were lower than in condition (1). This reduction is caused by

partial removal of the insulating oxide layer. No shift of the entire spectrum due to surface charging was observed. The peak ratio of Cd:Si:As was 0.4:0.8:2, indicating a better surface stoichiometry. The carbon peak appeared much larger than in condition (1). The etching procedure may have left a large quantity of carbon (particles?) on the crystal surface. The surface contamination by oxygen dropped from 10 at% in condition (1) to 2 at% in condition (2).

Following procedure (3), the oxygen contamination of the surface dropped further to 0.6 at%, and the carbon contamination was reduced from 51 at% in condition (2) to 21 at% in condition (3). The Si and As peaks were no longer shifted toward higher energies, indicating that they are no longer bound to oxygen, but rather bound covalently in the crystal. The surface ratio is estimated at Cd:Si:As = 0.7:1.4:2. This suggests a preferential ion etching of arsenic.

4. Summary

$CdSiAs_2$ single crystals with a p-doping level ranging from 10^{13} cm^{-3} to 10^{16} cm^{-3} (appropriate for solar cell and photocathode investigations) could be grown by the chemical vapor transport technique, employing halogens as transport agents. Doping procedures, using boron or aluminum as a doping agent, were formed to raise the net acceptor level up to 10^{18} cm^{-3}. The crystals showed room-temperature Hall mobilities up to 300 cm^2/V s. The carrier compensation degree K ranged from 0.02 to 0.47. The acceptor activation energies as a function of the net acceptor density follow the law $E_A(p) = E_A(0) - \alpha p^{\frac{1}{3}}$ yielding $E_A(0) = 310$ meV and $\alpha = 6.7 \times 10^{-4}$ meV/cm. The results of the photoluminescence investigation are in good agreement with previous results; they especially

confirm the previously assumed band structure. The XPS measurements showed that etching of the crystal surface with HF removes a Si-rich oxide layer from the surface; the surface stoichiometry is, therefore, improved. Probably, ion etching leads to a preferential removal of As atoms. A problem is the carbon at the surface: careful rinsing and storing of the crystals is necessary to avoid additional carbon contamination.

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References

[1] A. S. Borshchevskii, N. A. Goryunova, F. P. Kesamanly and D. N. Nasledov, Phys. Stat. Sol. **21** (1967) 9.

[2] N. A. Goryunova, in Proc. of the 9th Int. Conf. on the Physics of Semiconductors, Moscow, July 23–29, 1968.

[3] J. L. Shay and J. H. Wernick, *Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications,* Pergamon Press, Oxford, 1975.

[4] V. D. Prochukhan and Yu. V. Rud, Sov. Phys. Semicond. **12** (1978) 121.

[5] Ch. Dovletmuradov, K. Ovezov, V. D. Prochukhan, Yu. V. Rud and M. Serginov, Sov. Phys. Semicond. **10** (1976) 986.

[6] A. F. Carroll, C. F. Smith, L. C. Burton and L. H. Slack, Rev. Electrochem. Soc. **128** (1981) 8.

[7] P. Zürcher and F. Meier, J. Appl. Phys. **50** (1979) 3687.

[8] C. K. Sinclair, J. de Physique **46** (1985) C2-699.

[9] M. Kimmel, M. Lux-Steiner, M. Võgt and E. Bucher, J. Appl. Phys. **64(3)** (1988) 1560.

[10] C. F. Smith, L. C. Burton, A. F. Carroll and L. H. Slack, Thermochimica Acta **40** (1980) 235.

[11] A. S. Borshchevskii, Yu. A. Valov, N. A. Goryunova, E. O. Osmanov, S. M. Ryvkin and G. P. Skpen'kov, Sov. Phys. Semicond. **2** (1969) 1145.

[12] J. L. Shay and E. Buehler, Phys. Rev. **B3** (1971) 2598.

[13] M. Avirović, M. Lux-Steiner, U. Elrod, J. Hönigschmid and E. Bucher, J. Crystal Growth **67** (1984) 185.

[14] M. Kimmel, *Herstellung und Untersuchung von $CdSiAs_2$-Einkristallen,* Hartung-Gorre Verlag Konstanz, 1988.

[15] A. J. Spring-Thorpe and B. R. Pamplin, J. Crystal Growth **3** (1968) 313.

[16] G. K. Averkieva, N. A. Goryunova, V. D. Prochukhan and M. Serginov, Sov. Phys. Doklady **15** (1970) 386.

[17] Ch. Kittel, *Introduction to Solid State Physics*, John Wiley and Sons Inc., New York, 1986.

[18] G. G. Baumann, Ph.D. thesis, University of Konstanz, 1983 (FRG).

[19] T. Woike, private communication.

[20] F. W. Schmidlin and G. G. Roberts, Phys. Rev. Lett. **20** (1968) 1173.

[21] M. Toyoma, K. Unno and M. Naito, Jap. J. Appl. Physics **8** (1969) 1118.

[22] A. Möschwitzer and K. Lunze, *Halbleiterelektronik*, Dr. Alfred Hüthig Verlag, Heidelberg, 1980.

[23] G. L. Pearson and J. Bardeen, Phys. Rev. **75** (1949) 865.

[24] P. P. Debye and E. M. Conwell, Phys. Rev. **93** (1954) 693.

[25] A. C. Bebb, *Photoluminescence I: Theory* in *Semiconductors and Semimetals 8,* R. K. Willarson, ed., Academic Press, New York, 1972.

[26] G. K. Averkieva, N. A. Goryunova, V. D. Prochukhan, S. M. Ryvkin, M. Serginov and Yu. G. Shreter, Sov. Phys. Semicond. **5** (1971) 155.

[27] I. A. Mal'tseva, V. D. Prochukhan, Yu. V. Rud and M. Serginov, Pis'ma Zh. Tekh. Fiz. **12** (1976) 385.

[28] A. Mamedov, Z. A. Parimbekov, Yu. V. Rud and M. Serginov, Sov. Phys. Semicond. **16** (1982) 465.

[29] Y. P. Varshni, Physica **34** (1967) 149.

[30] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy,* Perkin-Elmer Corporation, Minnesota, 1979.

TABLE 1

Detected Cd, Si and As peaks (eV), in comparison with relevant literature data [30]. Numbers in brackets refer to the surface conditions, as explained in the text. All binding energies (± 0.5 eV) are given with respect to the C 1s peak at 285.0 eV.

	Cd 3d 5/2	Cd 3d 3/2	Si 2p	As 3d 5/2
(1)	405.0	411.5	103.5	44.0
(2)	405.0	411.5	101.0	42.0
(3)	405.0	412.0	100.4	42.0
CdO	404.0			
Cd	404.8			
$Cd(OH)_2$	404.9			
Si			98.6-99.5	
SiO_2			103.1-103.6	
GaAs				40.7
As				41.2-41.6
$C_{10}H_{21}AsOOH$				44-45

Figure Captions

1. Schematic representation of the growth ampoule and the three-zone-furnace temperature gradient used for the growth of the $CdSiAs_2$ single crystals.
2. Typical prismatic elongated $CdSiAs_2$ single crystals grown by cadmium chloride in the ampoule (mm grid).
3. Typical planar $CdSiAs_2$ single crystals grown by bromine (mm grid).
4. (a) Hall mobility and (b) net acceptor density of four different growth runs as a function of temperature: △ and • undoped, □ boron-doped and ○ aluminum-doped.
5. Acceptor activation energy as a function of the cubic root of the net carrier density, at room temperature: △ measured values and • calculated values.
6. Photoluminescence spectrum of $CdSiAs_2$ at liquid helium temperature. The insert in the right upper-corner shows the bandstructure at the Γ-point.
7. The bandgap energy A (△) and the assumed exciton transition energy E_1 (◇) as a function of the temperature.
8. XPS-spectra for surface conditions (1) solid line, (2) dashed line and (3) dot-dashed line.

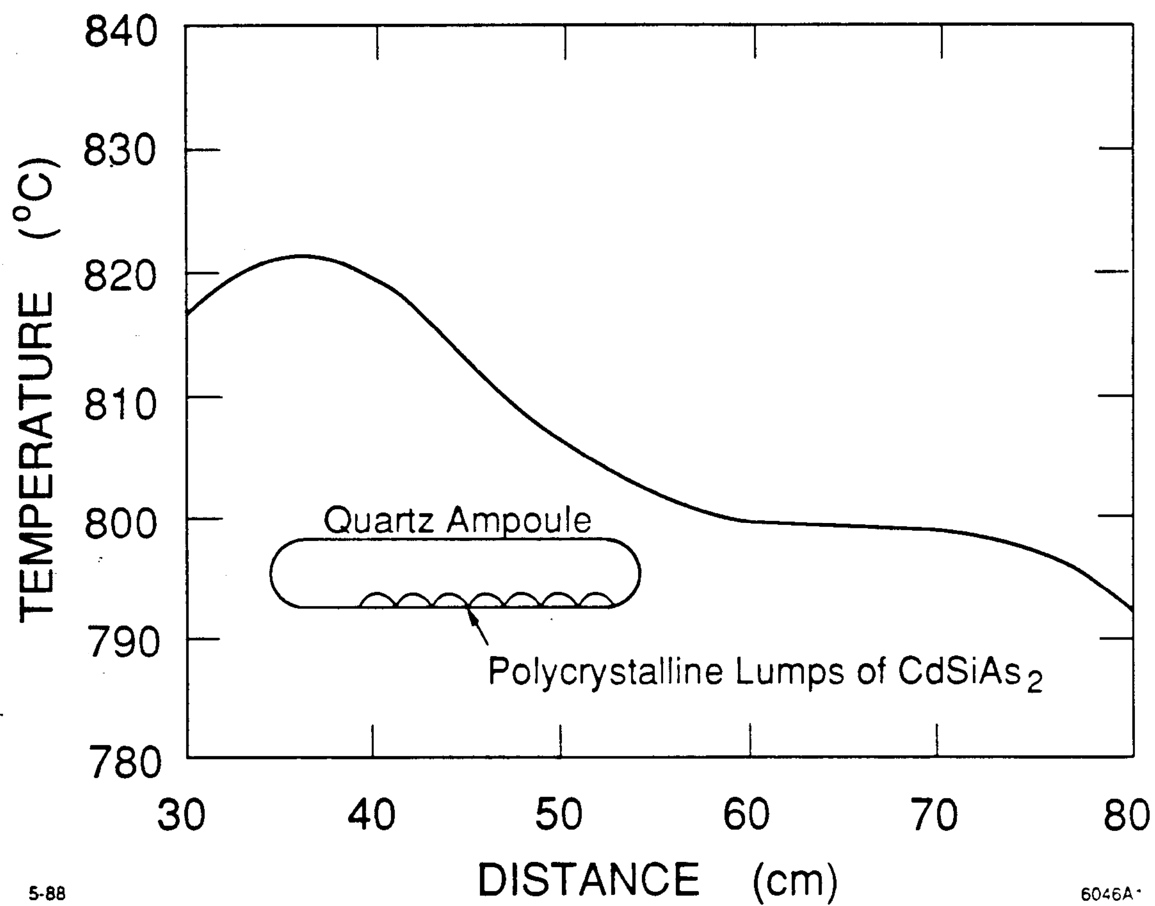

Fig. 1

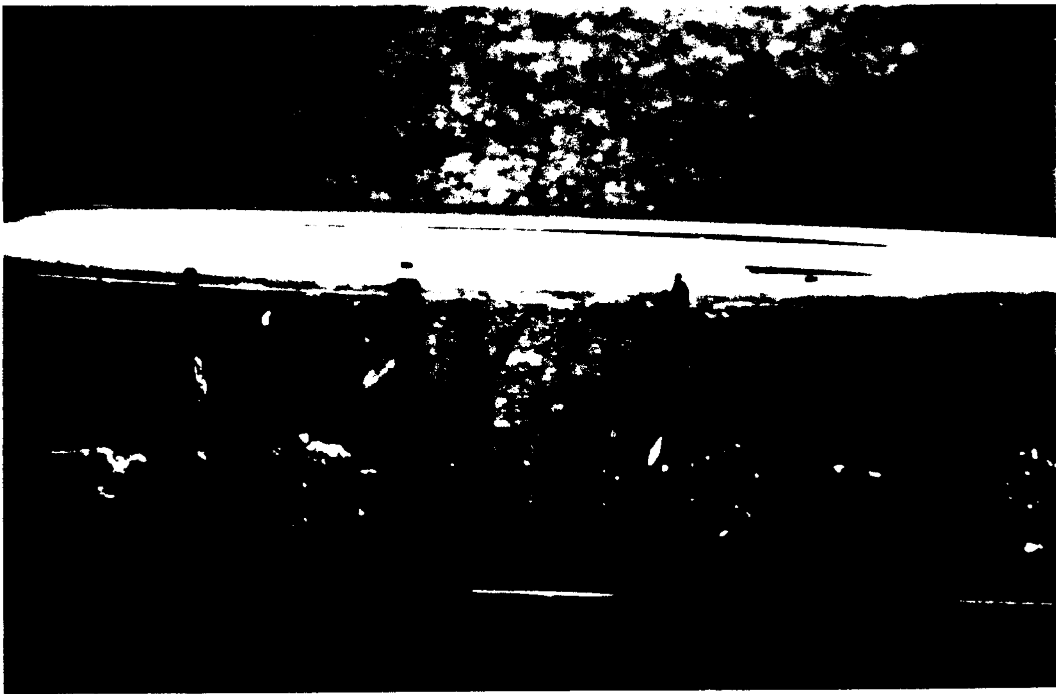

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Fig. 2

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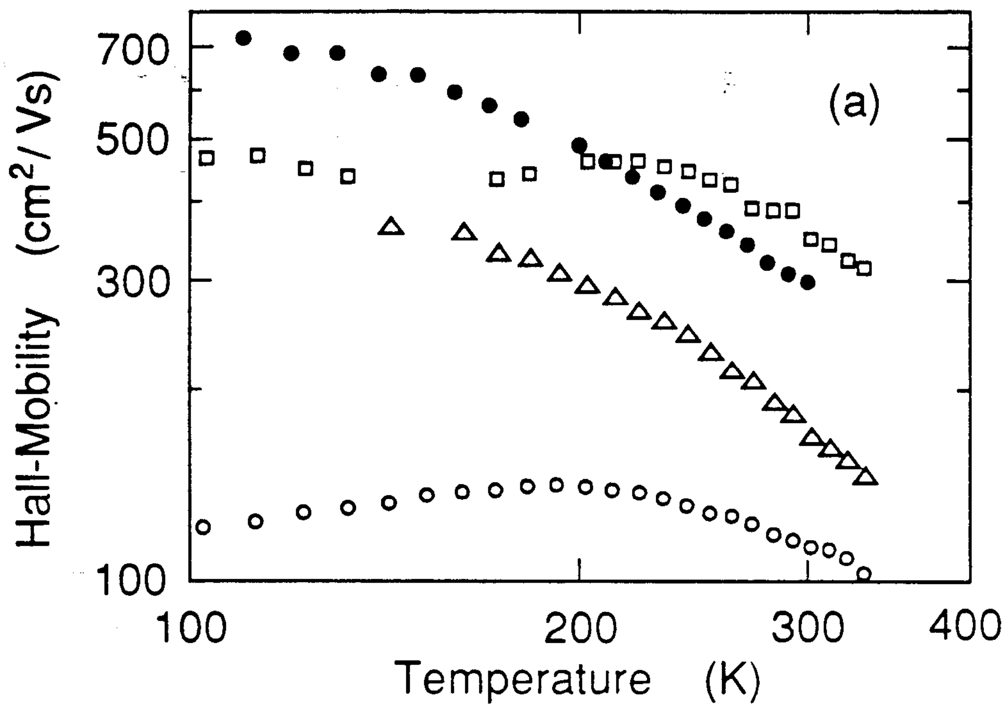
Fig. 3



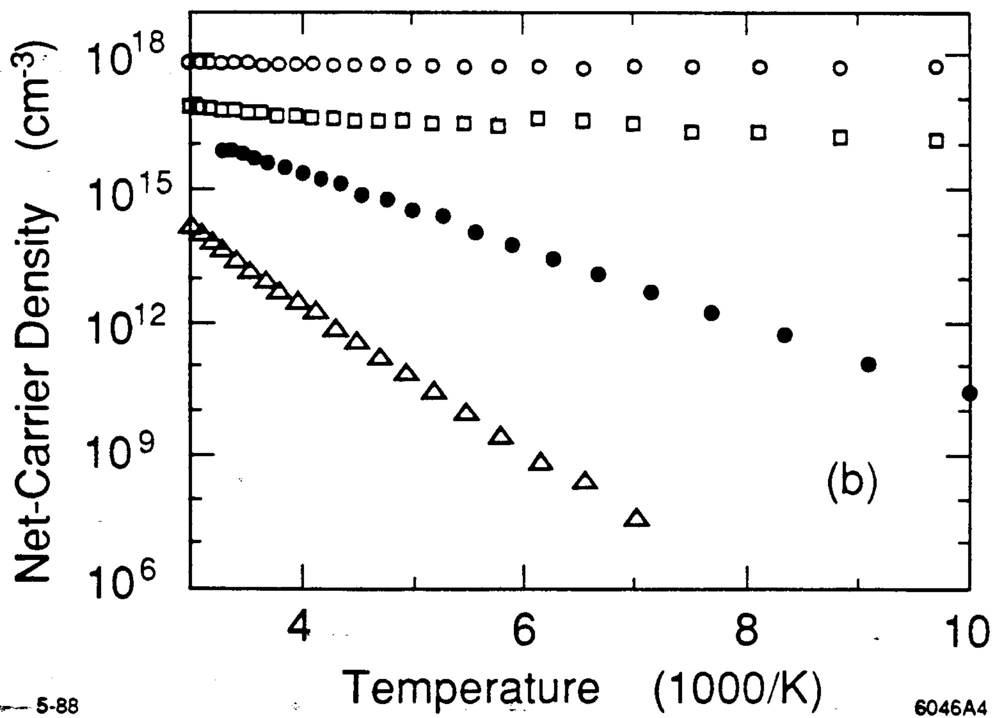


Fig. 4

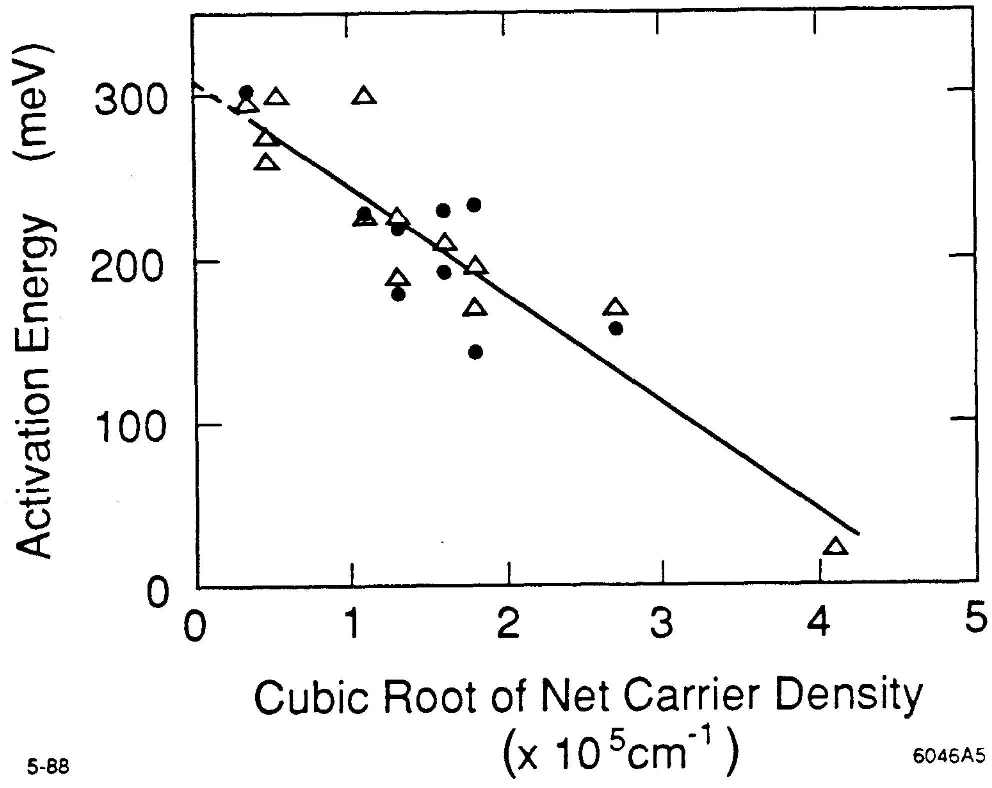


Fig. 5

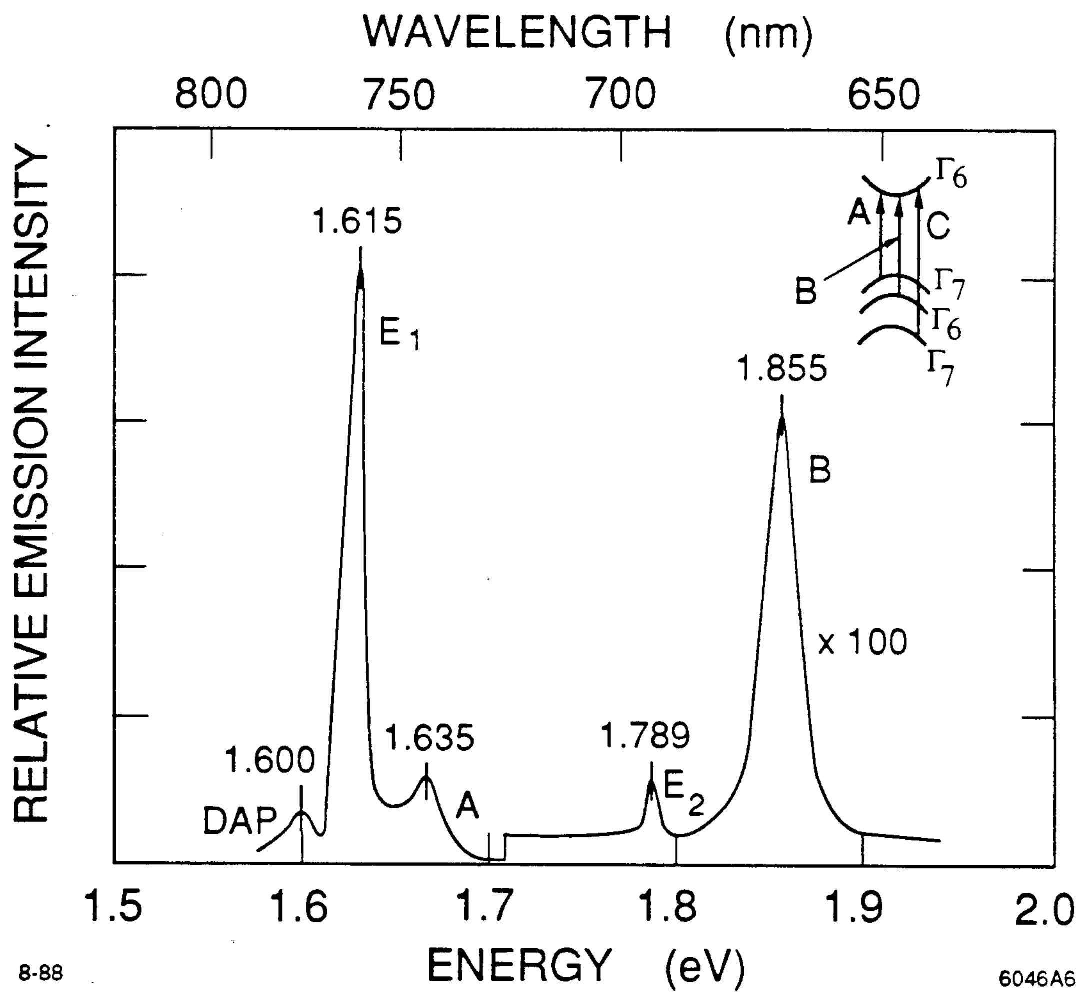


Fig. 6

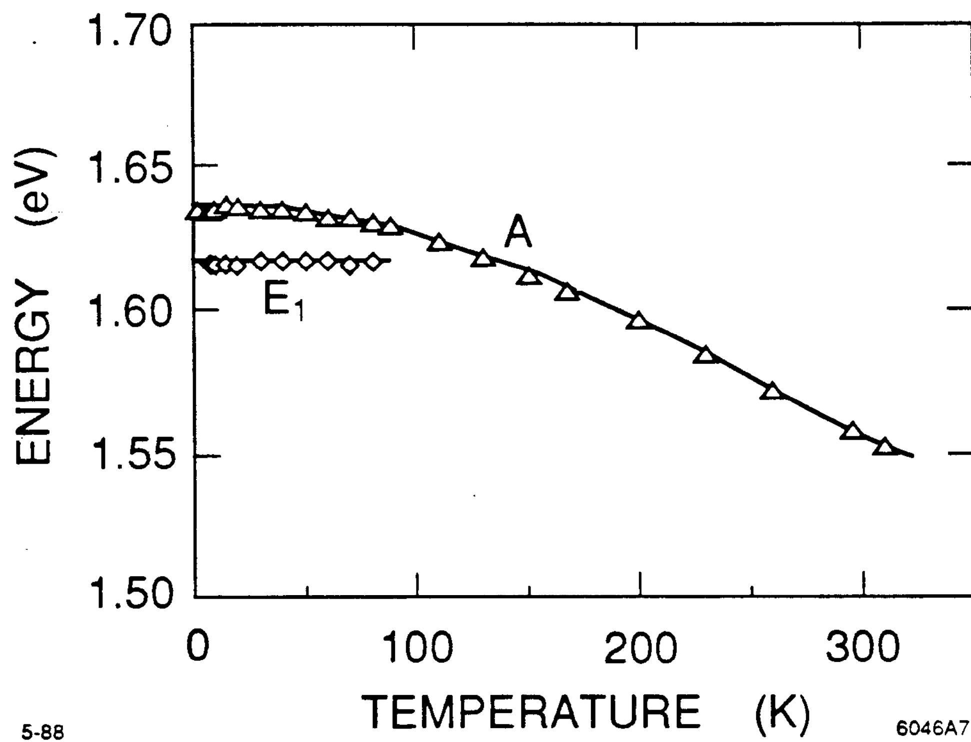


Fig. 7

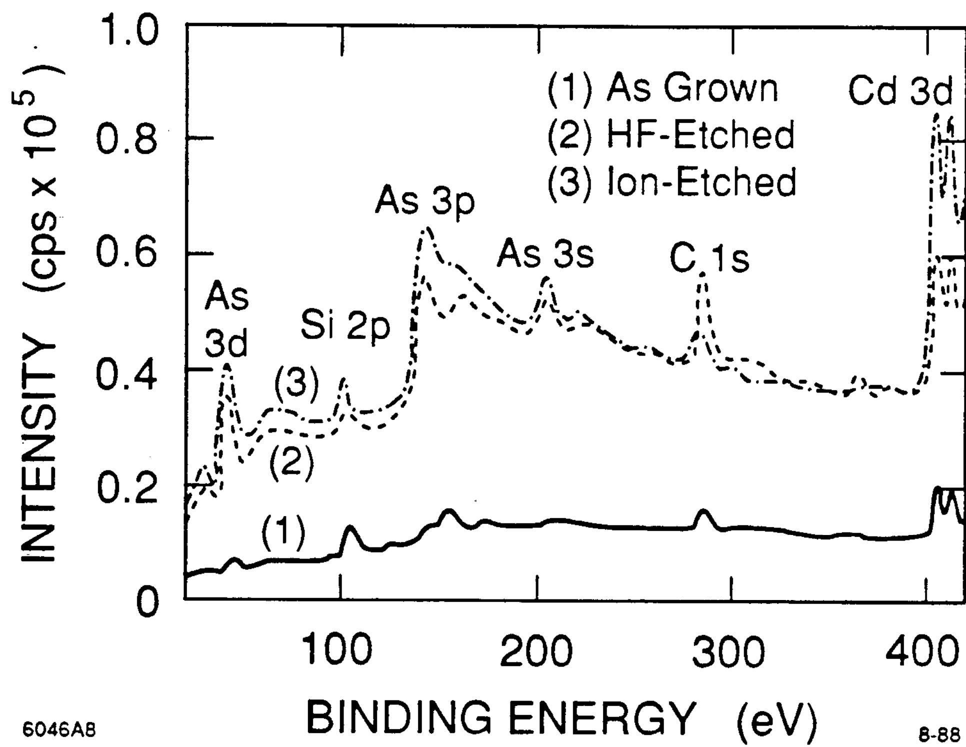


Fig. 8