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GROWTH OF IV-VI, II-VI AND III-V SEMICONDUCTOR COMPOUNDS BY HOT WALL EPITAXY

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Abstract. - In this work we present a summary of the latest results obtained in our lab on epitaxial layers of CdS, CdTe, Pb-salts, the semimagnetic compound Pb_{1-x}Mn_{x}Te and GaAs. These layers have been prepared using a relatively new evaporation method called Hot Wall Epitaxy (HWE). The main characteristic of this technique is its simplicity and the possibility to grow epitaxial layers under conditions closer to thermodynamic equilibrium than most other evaporation methods. The layers have been characterized using procedures like SEM, Hall-Effect and X-ray diffraction. The results prove that the properties of the layers obtained by HWE are nearly as good as those of bulk-material. Mono-crystalline PbTe samples were grown on BaF$_2$ with mobilities at 3x10$^4$cm$^2$/Vs at 77K for n-type and 1x10$^4$cm$^2$/Vs for p-type samples. We were able to grow Pb$_{1-x}$Mn$_x$Te (x=1-2%) samples with high mobility and low carrier concentration. Thin films of CdS and CdTe deposited on BaF$_2$, SrF$_2$ and bulk CdTe grew epitaxially on these substrates and had a grained structure. We obtained n-type films using Indium as a dopant. Electron concentration was typically 2x10$^{16}$cm$^{-3}$ in PbTe and 5x10$^{17}$cm$^{-3}$ in CdTe. Room temperature values of electron mobility of up to 230cm$^2$/Vs for CdS and 600cm$^2$/Vs for CdTe were obtained.

1. Introduction.- Thin epitaxial films of some of the most important semiconductor materials were grown with many different methods so far. Usually these layers suffer from their inferior electrical and optical properties when compared with bulk material. The Hot-Wall-Epitaxy (HWE) is a relatively new and inexpensive method for growing thin epitaxial films and our results demonstrate that it can substitute in many applications for other more complicated systems such as Sputtering and Molecular Beam Epitaxy. The main characteristic of this technique is its simplicity and the possibility to grow epitaxial layers under conditions closer to thermodynamic equilibrium than most other evaporation methods.

IV-VI compounds especially PbTe, SnTe and several series of mixed crystals like Pb$_{1-x}$Sn$_x$Te and Pb$_{1-x}$Ge$_x$Te in form of epitaxial layers have been the subject of consi-
derable attention, owing to their technological importance in the IR field. Some experiments in solid state basic research could be done only because of the high quality of the films obtained by HWE. The relatively new field of semimagnetic semiconductors is now stimulated in our group by the growth of thin layers of Pb\(_{1-x}\)MnxTe also fabricated in our laboratories. In principle the II-VI compounds are considered to be one of the best materials for the production of solar cells. The high efficiency of such solar cells depends mainly on the successful growth of low resistivity thin films. In this paper we present latest results obtained with HWE for CdTe and CdS. GaAs, one of the most important representative of the III-V compounds is widely used in the production of semiconductor devices such as photovoltaic detectors and high speed elements. Our preliminary results indicate that the HWE system can be used also for the epitaxial growth of GaAs layers.

2. Hot-Wall-Epitaxy.- In very simple terms we can say that the HWE is a vacuum film deposition technique whose main characteristic is the growth of epitaxial films under conditions as near as possible to thermodynamic equilibrium. One of the ways to accomplish this is by means of the apparatus shown schematically in Fig.1 for the case of CdTe. The system consists essentially of a heated quartz tube with three independent furnaces which allow the partial pressure of the CdTe, In and Cd source materials to be controlled separately. The substrate at the top closes the tube. The hot wall, held at the CdTe source temperature, serves to direct the evaporating atoms or molecules from the source to the substrate. In this manner, loss of material is avoided and a clean environment is kept inside the growth tube without using an ultra high vacuum system. Relatively high pressures of the evaporating materials can be maintained inside the tube and as a result, the difference between the source and the substrate temperature can be significantly reduced. Qualitatively one might expect a higher crystalline perfection via enhanced reevaporation of atoms or molecules from energetically unfavourable sites. Thus it is apparent, that HWE should be used in the closed-tube mode whenever possible. Some times as in the case of Pb\(_{1-x}\)MnxTe it is necessary to keep the substrate at some distance above the mouth of the tube to minimize the influence of the walloven on the substrate temperature. Under these conditions the main advantages of the HWE are somewhat diminished but not completely lost. However, with a good design of the quartz tube a well collimated beam can be produced, resulting in a high impingement rate on the surface of the substrate. The mentioned main advantages of the HWE system can also be approached by the use of the classical vapor deposition method. However, this method lacks the flexibility encountered in standard evaporation techniques. The HWE combines these two characteristics, i.e. growth near equilibrium conditions and versatility.

Fig.1: Schematic setup of a hot wall apparatus for the growth of CdTe including a compensating source for Cd.
3. Results.

a) IV-VI Compounds.- A concise summary of the growth conditions and the film properties is given in Table I.

Our results indicate that it is possible to grow consistently good films, using the same PbTe single source repeatedly, if an appropriate Te overpressure is maintained to compensate for the degradation of the single source. By adjusting the substrate temperature and Te overpressure, both n- and p-type films and also p-n junctions were fabricated. \( \text{(7)} \)

Mobilities obtained on BaF\(_2\) substrates were as high as 300000 cm\(^2\)/Vs at 77K and 8x10\(^5\) cm\(^2\)/Vs at 4.2K for n-type samples and 1x10\(^4\) cm\(^2\)/Vs at 77K for p-type samples.

All the films investigated were monocrystalline, as revealed by their Laue patterns. The layer thickness was in the range of 1-10\(\mu\)m. The surfaces of the films were examined with the aid of a scanning electron microscope. No noticeable surface structure was observed except for steps which reproduced the cleavage steps of the substrate material. \( \text{(8)} \)

As an example for the fabrication of materials for basic research we shall mention the growth of Pb\(_{1-x}\)Mn\(_x\)Te films for investigations in the upgrading field of semimagnetic semiconductors. Failure to perform such experiments in bulk material is attributed to the inability to prepare samples with high mobility together with low carrier concentration. \( \text{(9)} \)

In Fig.2 we show the carrier concentration versus the nominal Te pressure in the growth apparatus for some Mn temperatures. As a test for the good crystalline quality of the grown films we measured the mobility as a function of temperature. The results for

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**TABLE I**

**TYPICAL GROWTH CONDITIONS AND CHARACTERISTIC PARAMETERS OF SOME IV-VI COMPOUNDS**

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature ( ^\circ)C</th>
<th>( x )</th>
<th>Growth-rate ([\mu\text{m/h}])</th>
<th>Mobility ((300\text{K})) ( [\text{cm}^2/\text{Vs}] )</th>
<th>Carrier-concentration ( \times 10^{17} ) ( [\text{cm}^3] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTe</td>
<td>450</td>
<td>560</td>
<td>260-350 (Te)</td>
<td>/</td>
<td>1500</td>
</tr>
<tr>
<td>PbSe</td>
<td>460</td>
<td>550</td>
<td>/</td>
<td>/</td>
<td>1000</td>
</tr>
<tr>
<td>( \text{Pb}_{1-x} \text{Ge}_x \text{Te} )</td>
<td>470</td>
<td>560 (PbTe)</td>
<td>510 (GeTe)</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>( \text{Pb}_{1-x} \text{Sn}_x \text{Te} )</td>
<td>430</td>
<td>550 (PbSnTe)</td>
<td>570 (Pb)</td>
<td>20</td>
<td>4</td>
</tr>
<tr>
<td>( \text{Pb}_{1-x} \text{Mn}_x \text{Te} )</td>
<td>510</td>
<td>645 (PbTe)</td>
<td>750 (Mn)</td>
<td>1-2</td>
<td>2</td>
</tr>
</tbody>
</table>

\( \text{§)} \text{Because of the small energy gap of Pb}_{1-x} \text{Sn}_x \text{Te only values at low temperatures are significant.} \)
three different Pb$_{1-x}$Mn$_x$Te samples with different Mn concentrations are shown in Fig. 3. In the range 300-400K, the mobility curves have a slope in the neighbourhood of 5/2, typical for IV-VI materials. Below 40K the mobilities tend to saturate at values depending on the Mn concentration.

![Graph showing Hall mobility and carrier concentration vs. temperature for Pb$_{1-x}$Mn$_x$Te samples with different Mn concentrations.](image)

Fig. 3: Temperature dependence of the Hall mobility and the carrier concentration for some Pb$_{1-x}$Mn$_x$Te films with different Mn concentrations.

b) II-VI Compounds. - The growth conditions and characteristic parameters for CdTe and CdS films are collected in Table II. It was established that the most important factors affecting the structure of the films were the nucleation and growth process of the first monolayers. These factors determine essentially the crystalline structure of the subsequent deposited layers. So the growth rate is not only a function of the supersaturation but also a function of the defect structure of the films. The crystalline quality was examined by X-ray diffraction. The result for a CdS sample grown with a substrate temperature of 500°C is depicted in Fig. 4a.

### Table II
TYPICAL GROWTH CONDITIONS AND CHARACTERISTIC PARAMETERS OF SOME II-VI COMPOUNDS

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature [°C]</th>
<th>Growth rate [μm/h]</th>
<th>Mobility$^1$ [cm²/V·sec]</th>
<th>Carrier concentration [300K] [cm⁻³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-CdTe</td>
<td>Substrate: 480</td>
<td>Material 1: 580</td>
<td>Dopant: 590 (In)</td>
<td>Material 2: 260 (Cd)</td>
</tr>
<tr>
<td>CdS</td>
<td>Substrate: 550</td>
<td>Material 1: 630</td>
<td>Dopant: 550 (In)</td>
<td>-</td>
</tr>
</tbody>
</table>

a) Maximum values obtained in as-grown layers.
In only a part of the temperature interval investigated. The first type corresponds to Fig. 5a. In the temperature region of 300K to approximately 100K the mobility is dominated by grain boundary scattering. At temperatures below 100K the temperature dependence of \( \mu \) becomes very weak. In this case electron transport takes place probably by tunneling through the barrier. The second type is shown in Fig. 5b. In this case the mobility at high temperatures is governed by phonon scattering (\( \mu_{\text{ph}} \)). However, at low temperatures the influence of grain boundary scattering (\( \mu_{\text{b}} \)) is large enough in this sample so that bulk scattering mechanisms such as impurity scattering (\( \mu_{\text{i}} \)) do not play a significant role.

We noticed that in general for samples prepared under the same growth conditions there is a tendency for the mobility to decrease with decreasing carrier concentration peaks of CdS are as sharp as those of the monocrystalline BaF\(_2\) with a substrate temperature of a) 500°C b) 460°C. All investigated CdTe and CdS films were doped with In. As a result electron concentrations up to 2x10\(^{18}\) cm\(^{-3}\) in CdTe and 3x10\(^{18}\) cm\(^{-3}\) in CdS were obtained. At room temperature we measured mobilities of 600 cm\(^2\)/Vsec for CdTe and 230 cm\(^2\)/Vsec for CdS.

All our samples could be divided into two groups: a) those where grain boundaries dominate the scattering mechanism in the whole temperature range studied; b) those where the grain boundaries play no role at all or determine the mobility in only a part of the temperature interval investigated. The first type corresponds to Fig. 5a. In the temperature region of 300K to approximately 100K the mobility is dominated by grain boundary scattering. At temperatures below 100K the temperature dependence of \( \mu \) becomes very weak. In this case electron transport takes place probably by tunneling through the barrier. The second type is shown in Fig. 5b. In this case the mobility at high temperatures is governed by phonon scattering (\( \mu_{\text{ph}} \)). However, at low temperatures the influence of grain boundary scattering (\( \mu_{\text{b}} \)) is large enough in this sample so that bulk scattering mechanisms such as impurity scattering (\( \mu_{\text{i}} \)) do not play a significant role.

We noticed that in general for samples prepared under the same growth conditions there is a tendency for the mobility to decrease with decreasing carrier concentration.

![Fig. 4: X-ray diffraction spectra for CdS films grown on monocrystalline BaF\(_2\) with a substrate temperature of a) 500°C b) 460°C.](image1.png)

![Fig. 5: Temperature dependence of the Hall mobility for CdS films.](image2.png)
tion. This behaviour can be explained by means of a grain boundary model proposed by Kamins. \(^{(1)}\) The validity of this assumption was proved by our investigations, done by annealing experiments in a dynamic vacuum. \(^{(12)}\)

c) III-V Compounds.- The ranges over which the temperature in the growth apparatus were varied are the following: 900 - 925°C for the GaAs source; 930 - 950°C for the Ga source and 560 - 610°C for the substrate. At substrate temperatures higher than 625°C a rough surface of the layers was obtained. The rates of growth varied from 1-2 μm/h.

As a first test of the crystalline quality we performed X-ray diffraction measurements. The results, depicted in Fig. 6, showed sharp peaks as well for the SrF₂ substrate as for the GaAs layer. Even the splitting of the lines due to the used Cu-Kα radiation is clearly reproduced in the GaAs peaks. After progress of growing reproducible GaAs layers with a certain set of growth parameters, we are now working in the problem of doping the material with Te or Sn.

4. Conclusion.- It is obvious from this short summary of the work done in our laboratories that the HWE method has contributed decisively to the upgrading of the quality of thin films of those materials for which it has been used. It is our opinion that despite the improvements brought about by HWE the full possibilities of this method have still not been realized. Therefore we have already begun to perform systematic studies towards a full characterization and understanding of HWE.

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