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Chemical Vapor Deposition and Properties of GaAs on Molybdenum Substrates

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Abstract

The chemical vapor deposition of GaAs on metallurgical grade molybdenum, using trimethylgallium and arsine in hydrogen was studied toward the realization of cost effective solar cells for terrestrial applications. The influences of substrate temperature, reactant mole fractions and H₂S dopant on the microstructural properties of the deposited layers were studied using X-ray diffraction and scanning electron microscopy. X-ray diffraction analysis showed that the GaAs films were randomly oriented with a (220) preferred orientation parallel to the substrate. The grain size of GaAs crystallites in the range from 1 to 4 μm increased with increasing substrate temperature, up to 950°C, where molybdenum and arsenic formed reaction products on the substrate. Growth rates at different concentrations of trimethylgallium showed evidence for an incubation time required for the nucleation of GaAs on Mo. The introduction of a H₂S dopant with mole fraction below 2×10⁻⁴ was found to have no significant influence on the morphology of GaAs films.

Work performed under the auspices of the U. S. Energy Research and Development Administration.
Introduction

GaAs is one of the most promising semiconducting compounds for the preparation of terrestrial solar cells: its favorable band gap energy in relation to the solar energy spectrum results in the highest predicted photovoltaic conversion efficiency, its high absorption coefficient is such that a layer of a few microns in thickness is sufficient to absorb almost all of the incident sunlight, implying a low consumption of material in solar cells. Also, this compound can be used at a significantly higher temperature than its competitors without an important loss of conversion efficiency, thereby minimizing the cooling problem during the operation of the cells in conjunction
with concentrators.

Single crystal solar cells have been prepared using GaAs\textsuperscript{1} but they are economically unattractive, owing to the high cost of gallium, and to the high technological cost of liquid-phase epitaxial growth. For terrestrial applications of solar cells, the vapor phase deposition of a thin layer of GaAs on a low-cost substrate offers significant simplification and cost reduction of the finished solar cell. The absorption coefficient of GaAs is sufficiently high that only a thin layer 3-5 \(\mu\)m thick is sufficient to absorb most of the solar spectrum with energy in excess of the band gap.\textsuperscript{2} Also, it has been shown recently that a GaAs grain size in the range of 3-5 \(\mu\)m would be sufficient to attain 90\% of the maximum conversion efficiency.\textsuperscript{3}

A recent review of potential, low-cost substrates for GaAs solar cells has shown that molybdenum has several advantages over other metals.\textsuperscript{4} Molybdenum is available at a reasonable cost, has a thermal expansion coefficient close to that of GaAs and it has a volatile oxide which can be easily removed during the GaAs growth process. This metal was selected for study as a substrate for GaAs solar cells in spite of the high contact resistance with GaAs.\textsuperscript{5}

The object of this study is to explore the influence of growth conditions on film properties toward producing thin films of GaAs on molybdenum which satisfy the requirements for high efficiency solar cells, and to study the microstructural and electrical properties of the deposited films. The depositions of GaAs by chemical vapor deposition (CVD) using the system Ga(CH\textsubscript{3})\textsubscript{3} (TMG)/AsH\textsubscript{3}/H\textsubscript{2} is described.
To date, this method of preparation appears to be most attractive for the large scale fabrication of solar cells.2

Experimental

Apparatus - The experimental apparatus for chemical vapor deposition studies consisted of a stainless steel and pyrex flowmetering system and a water-cooled, 5.1 cm OD vertical reaction tube 30 cm in length. Metal substrates were supported on a 2.5 cm diameter pyrolytic graphite disk susceptor which was inductively heated. The TMG was contained in a pyrex and stainless steel sparging tube cooled to 0°C through which a metered flow of H₂ was passed. The hydrogen carrier gas was purified by a Matheson Model 8362 purifier before mixing with metered quantities of AsH₃, TMG and dopant gases in a pyrex mixing vessel. The flowmetering system contained connections for evacuating the system, purging with helium or hydrogen, and for bypassing the reactor to vent. A schematic of the growth apparatus is shown in Fig. 1.

Materials - The reagent materials used in this study were electronic grade TMG obtained from Ventron, and pure arsine and dopant gas mixtures obtained from Matheson Gas Products.

The pyrolytic graphite susceptor, obtained from Poco Graphite were specially treated with high-temperature HCl in order to remove metallic contaminants. Metal substrates used in deposition studies were 1.5 mm thick plate with a purity of >99.95%. The grain size of surface grains was approximately 5 µm, elongated slightly in the rolling direction.
**Procedure** - The metal substrate and the graphite susceptor were thoroughly degreased by boiling for 10 min. each in perchoroethylene, acetone, methanol and isopropyl alcohol. Samples were then chemically polished in a 6:2:1 mixture of lactic:nitric:hydrofluoric acids. Immediately before the deposition, a final cleaning with a dichlorodifluomethane gas stream was applied. The susceptor and sample were then placed in the reaction tube which was successively purged with helium and then hydrogen. A total flow rate of 1 liter/min was used in experimental runs.

At the end of helium and hydrogen purge periods, the sample and susceptor were annealed as about 1000°C for 10 min. in hydrogen to reduce possible oxides at the surface of the molybdenum. This process also allowed desorption of gases from the graphite susceptor. Then the temperature was reduced to the deposition temperature and the flows of arsine dopant gas and TMG were sequentially started. At the end of the deposition process, the flow of TMG and \( \text{H}_2\text{S} \) were stopped and the temperature reduced to about 350°C. The arsine flow was then stopped and the system allowed to cool under hydrogen to room temperature. The substrate was finally removed after a helium purge.

The concentration of TMG in the input gas was calculated on the assumption that equilibrium was reached at all times in the TMG saturator. The saturator was designed to maximize the contacting between the gas and liquid phases. Raoult's law was assumed to be a valid description of the \( \text{H}_2\text{-TMG} \) equilibrium. The vapor pressure of TMG at 0°C was taken from the literature to be 8.60 kPa (64.5 Torr).
Results

The chemically vapor deposited GaAs films were studied to determine the effect of growth conditions, such as substrate temperature, reactant mole fractions and $H_2S$ dopant concentration, on the microstructure and electrical properties of the films. In most experiments, the deposition time was adjusted to produce GaAs films with thickness between 1 and 5 $\mu m$, while in other experiments films with thickness between 10 and 30 $\mu m$ were produced to explore the dependence of grain size on film thickness. All films were examined by scanning electron microscopy and X-ray diffraction analysis to determine the microstructural information.

**Microstructure of GaAs Films on Mo**

X-ray diffraction analysis showed that the GaAs films deposited on chemically polished Mo sheet substrates were randomly oriented with a preferred (220) orientation parallel to the substrate. All GaAs films were polycrystalline with grain size in the range from 1 to 5 $\mu m$, depending on the growth condition.

The grain size dependence on film thickness was investigated by sectioning and etching thick GaAs films on Mo. Samples were cut with a diamond saw, polished to 1 $\mu m$ diamond paste, and etched in a solution of 1% bromine in methanol. A scanning electron micrograph of the cross section of a 30 $\mu m$ GaAs layer deposited at 800°C with the TMG mole fraction, $y_{TMG} = 0.0017$, and arsenic to gallium input ratio, $As/Ga = 24$ is shown in Fig. 2. The substrate interface can be seen at the bottom of the figure. The average grain size at the Mo substrate is approximately 1.5 $\mu m$. With increasing distance from the substrate, the grain...
size increases, so that at the top surface of the film, grains larger than 4 μm in diameter are found. There is an absence of a columnar structure in the film, indicating continuous nucleation of new GaAs grains on the growing surface.

**Effect of Substrate Temperature**

The effect of substrate temperature on the film properties was investigated within the range from 600 to 950°C. A comparison of the surfaces of approximately 5 μm thick films deposited at different substrate temperatures is shown in Fig. 3. The figure shows that the grain diameter increases with substrate temperature from less than 1 μm at 600°C to up to 5 μm at 875°C. At very high substrate temperature, above 950°C, molybdenum was observed to react with arsine. Figure 3 shows that in films deposited at this temperature reaction products have formed on the surface. The compound MoAs₂ has been identified in the film by analysis of X-ray diffraction patterns.

The increasing size of GaAs crystallites with increasing substrate temperature is probably the result of a lower stability of critical nuclei at the higher substrate temperature, and to higher surface diffusion rate causing increased subgrain coalescence at the higher growth temperatures.

A practical temperature range which appears suitable for preparation of films for solar cells is 700°C < T < 875°C.

**Effect of TMG Mole Fraction**

Figure 4 shows the effect of GaAs growth at different concentrations of TMG in the hydrogen carrier gas, for a substrate temperature
of 800°C. Higher concentrations of TMG were found to produce larger
crystallites, with a maximum grain size of 5-10 μm at $y_{\text{TMG}} = 0.001$. GaAs
layers obtained at such high concentrations of TMG were nonuniform in
thickness and grains were irregular, with increased porosity in the GaAs
layer. Such a film structure could result in technological problems
in the processing of solar cells. Thus, the optimum TMG partial pressure
range appears to be from 0.0004 to 0.001.

Growth rates of GaAs on molybdenum were compared to rates of growth
on (100) GaAs substrates cut 2° toward the [010], under the same growth
conditions. In these experiments, GaAs layers were deposited for a
fixed period of 15 min in separate runs using the same reactor conditions
for growth on (100) GaAs. The samples were then sectioned, and the
layer thickness measured by scanning electron microscopy. The results
are summarized in Table 1. These results show that the growth rates of
GaAs deposited on Mo at low TMG mole fractions (below $6 \times 10^{-3}$) are less
than the growth rates on (100) GaAs, where as at much higher TMG mole
fraction, the growth rates are higher on Mo.

It has been shown in a previous work that the nucleation rate of
GaAs on Mo is less dependent on the concentration of TMG than is the
growth rate, and that nucleation occurs preferentially on sharp
angles of surface grains of the substrate. These effects suggest that
at low TMG mole fractions, the deposition rates are smaller on Mo than
on (100) GaAs as a consequence of the larger activation barrier for
heterogeneous nucleation on the molybdenum surface. As a consequence
of the incubation time for GaAs nuclei to form on molybdenum, the
measured deposition rate should be smaller than the growth rate
measured on GaAs for the same growth period. At higher TMG mole fractions, the incubation time for nucleation on the molybdenum surface should be shorter; once a surface layer of GaAs crystallites has formed, growth occurs on a higher surface area than on (100) GaAs, and higher deposition rates are obtained.

**Effect of the Ga/As Ratio**

The molar ratio As/Ga, representing the ratio of the input flow rates of AsH$_3$ and Ga(CH$_3$)$_3$, was observed to have an influence on the properties of the deposited GaAs films, due to two different growth mechanisms. At low As/Ga ratios, dendritic growth occurred in competition with film growth as shown in Figs 5a and 5b. The GaAs film density was found to increase as the As/Ga ratio decreased. At sufficiently high As/Ga ratios, (above 25) dendritic growth was suppressed.

The spherical caps seen at the extremity of the dendrites in Fig. 5a and 5b have been identified by energy-dispersive X-ray analysis to be nearly pure gallium. This suggests that the dendritic growth was the result of a VLS (vapor-liquid-solid) mechanism, whereas film growth was obtained by a VS (vapor-solid) growth mechanism.

The minimum As/Ga ratio under which dendritic growth occurred was found to range from 12 to 30 depending on the growth conditions, and particularly on the mole fraction of TMG and of the H$_2$S dopant. Variations in the microstructure of the molybdenum substrate also appears to influence the critical As/Ga ratio required for dendritic growth.
Effect of $H_2S$ Dopant

Undoped GaAs samples were found to be n-type with a carrier concentration of about $5 \times 10^{16}$ cm$^{-3}$. This carrier concentration was deduced from voltage breakdown measurements without correction for the presence of grain boundaries. This relatively high doping level is the consequence of diffusion of impurities contained in the substrate and of the high ratio As/Ga during the growth.

Samples intentionally doped by introducing $H_2S$ during the growth were n-type. Doping level were found to depend on the growth conditions and to be significantly influenced by contamination from the substrate. Higher deposition temperatures and slower deposition rates increased the effect of out-diffusion of impurities from the substrate, and thus produced higher carrier concentrations in the GaAs films. However, in a set of experiments performed under the same growth conditions with variation only in the flowrate of $H_2S$, the carrier concentrations were found to vary linearly on a log-log scale with the concentration of $H_2S$ over several orders of magnitude. These results show that doping level in the GaAs film can be controllably set.

The introduction of $H_2S$ during the growth process was found to have no significant influence on the morphological properties of the films, for $H_2S$ mole fractions up to $2 \times 10^{-4}$. This mole fraction was an order of magnitude larger than the maximum mole fraction of $H_2Se$ (about $3 \times 10^{-5}$) which could be introduced under similar growth conditions without affecting the microstructure of the GaAs films.
Conclusions

Polycrystalline GaAs layers have been deposited on polycrystalline molybdenum sheet by pyrolysis of Ga(CH₃)₃ and AsH₃, for application to terrestrial solar cells. Characteristics of the growth process and the properties of deposited films were studied.

GaAs deposited on chemically polished molybdenum sheet were polycrystalline, with randomly oriented and randomly disposed grains without a columnar structure, with grain size between 1 and 5 μm.

Increasing substrate temperatures up to 875°C produced larger GaAs crystallites. At higher temperature (above 950°C), molybdenum and arsenic were found to react to form MoAs₂ in the substrate.

Larger input concentrations of TMG produced larger GaAs crystallites but also a more roughened surface of the deposited film. At low TMG concentrations, GaAs growth rates on Mo substrate were smaller than on (100) GaAs substrate because of an incubation time required for nucleation, while at high TMG concentration, the growth rates on Mo were higher than on (100) GaAs.

The As/Ga molar ratio must be sufficiently large (12 to 30) to stabilize lateral growth of surface crystallites.

The introduction of H₂S during the growth process was found to have no significant influence on the morphology of the GaAs film deposited, for TMG mole fractions below 2×10⁻⁴. GaAs films grown with H₂S are n-type, and the carrier concentration varies linearly with the partial pressure of H₂S on a log-log scale.
Table 1. Comparison of GaAs Deposition Rates on Mo and (100) GaAs at 800°C.*

<table>
<thead>
<tr>
<th>Input Ga(CH₃)₃ mole fraction × 10³</th>
<th>Deposition Rate, µm/s(µm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo Substrate</td>
</tr>
<tr>
<td>0.41</td>
<td>0.0042(0.25)</td>
</tr>
<tr>
<td>0.87</td>
<td>0.0223(1.34)</td>
</tr>
<tr>
<td>1.72</td>
<td>0.0633(3.80)</td>
</tr>
</tbody>
</table>

*Experimental conditions:
- H₂ flow rate: 16.7 cm³/s (1 l/min)
- AsH₃/Ga(CH₃)₃ ratio = 24
REFERENCES

6. R. S. Crouse, Metallographic Appendix, Oak Ridge National Laboratory.
Fig. 1. Schematic diagram of the apparatus for chemical vapor deposition of GaAs.
Fig. 2. Scanning electron micrograph of the mechanically polished and chemically etched cross section of GaAs deposited on molybdenum at 800°C with $y_{\text{TMG}} = 0.0017$, and As/Ga = 24.
Fig. 3. Scanning electron micrograph of GaAs layers deposited on molybdenum at different substrate temperatures. The growth time was 15 min, As/Ga = 24, and $y_{H_2S} = 1.6 \times 10^{-5}$. (a) 600°C, (b) 700°C, (c) 875°C, (d) 950°C.
Fig. 4. Scanning electron micrograph of GaAs layer deposited on molybdenum different TMG mole fractions. The deposition was carried out at 800°C for As/Ga = 32, and $y_{H_2S} = 1.6 \times 10^{-5}$.

The TMG mole fractions and growth times are: (a) 0.018, 30 min; (b) 0.041, 15 min; (c) 0.087, 15 min; (d) 0.17, 5 min.
Fig. 5. Scanning electron micrograph of GaAs films deposited on molybdenum, with different As/Ga ratios. Deposition conditions are \( T_s = 800°C \), \( y_{\text{TMG}} = 4.1 \times 10^{-4} \), \( y_{\text{H}_2\text{S}} = 2.2 \times 10^{-5} \). The As/Ga ratios and deposition times are: (a) 12, 6.8 min; (b) 24, 10 min; (c) 29, 15 min.
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