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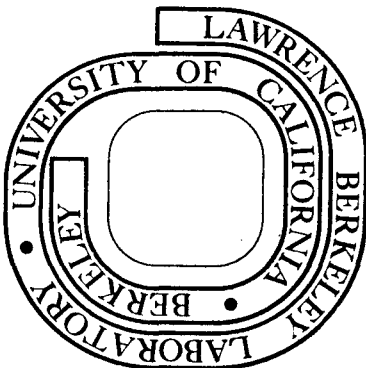
Rémy Christian de Bernardy-Sigoyer
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PROCESSING OF POLYCRYSTALLINE GaAs SOLAR CELLS

BY

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I. GENERAL INTRODUCTION

Now that the energy crisis has become a permanent reality, there is a strong incentive to develop alternate energy sources other than the conventional sources.

Solar cells, generating electricity directly from the sun by the photovoltaic effect, are a promising non-polluting alternate source. Among the suitable semiconducting compounds for use in the fabrication of solar cells, GaAs is one of the most attractive: its 1.4 eV band gap energy is close to the value which produces the maximum conversion efficiency of the solar irradiance; its absorption coefficient is such that a layer of only a few microns could absorb almost all incident sunlight; GaAs solar cells can work at a sensibly higher temperature than cells made with other materials without important loss of efficiency.

Single crystal GaAs solar cells have already been prepared, and conversion efficiencies up to 21% AM1 have been achieved, but they remain economically unattractive for terrestrial application in great part due to the high current price of GaAs and to the large mass of substrate needed for each cm^2 of solar cell.

In the cells prepared using single crystal substrates, the active part of the device is located in the first few top microns, with the remaining part being used just as a mechanical substrate. Thus, a cell consisting of a thin layer of GaAs (2-5 μm) deposited on a foreign material of low cost such as a metal or graphite would be much more

attractive from an economic point of view due to the much smaller amount of GaAs needed to make it, provided the performance of the cell were preserved.

In depositing GaAs on a foreign material, the film obtained is expected to be polycrystalline. The effect of the grain boundaries on the performances of the cell have been recently discussed and confirmed experimentally: due to the low diffusion length of the generated carriers in GaAs, a technology capable of producing grains of a few microns (2-5 μm) diameter with a comparable thickness and columnar in structure, would result in cells having a conversion efficiency close to that of single crystal cells.

This work is directed at obtaining thin films of GaAs having the properties required for low-cost solar cells, and at determining the properties of the deposited films. To prepare the films, the chemical vapor deposition technique has been preferred to liquid phase epitaxy. At that moment, the system $\text{Ga}(\text{CH}_3)_3/\text{AsH}_3/\text{H}_2$ appears to be the most attractive with respect to large scale production: this system is halogen-free (limiting corrosion problems), deposition is limited to a hot surface where the pyrolytic decomposition of $\text{Ga}(\text{CH}_3)_3$ can take place (implying low loss of material) and only one high temperature is required. For these reasons, this system has been chosen to prepare the experimental films.

In Chapter II, a comparison of the properties of different materials suitable as substrates for low-cost GaAs solar cells is presented. On the basis of this review, graphite and molybdenum were

selected for further study. The influence of the growth conditions (temperature, concentration of reactants, concentration of dopant gas) on the microstructural properties of deposited films of GaAs on graphite and molybdenum substrates are then reported in Chapter III and IV, respectively. Finally, the properties of GaAs solar cells prepared on molybdenum substrates are reported in Chapter V.

II. EVALUATION OF SUBSTRATE MATERIALS FOR LOW COST GaAs SOLAR CELLS

A. Abstract

GaAs has been deposited on substrate materials by chemical vapor deposition from trimethyl gallium and arsine in a hydrogen carrier gas. The microstructural and electrical properties of the films were studied to determine the effects of the different substrate materials on film and interfacial properties. Of particular interest were the grain size and growth morphology of GaAs crystallites, the interfacial reaction products formed between the GaAs and the metal during growth, and the resulting electrical contact resistance between the film and metal.

B. Introduction

Gallium arsenide has been shown to offer significant potential for use in high efficiency solar cells.¹⁻³ Although GaAs solar cells with highest efficiency have been prepared on single crystal substrates by liquid phase epitaxy,⁴ such cells remain economically unfeasible for large-scale terrestrial applications because of the high cost of gallium and the cost of the technology involved. Thin film solar cell technology, consisting of the deposition of a thin film of GaAs 2-5 μm thick on a low-cost substrate, is a potentially economical way to reduce the cost of solar cell production as well as reduce significantly the cost of the raw materials. The object of this chapter is to evaluate the properties of several substrate materials potentially useful in the

preparation of GaAs solar cells. A literature survey in conjunction with experimental deposition of films is presented, and on the basis of this study, different substrates are selected for further study.

C. Literature Survey

Several low-cost materials have been examined previously as substrates for polycrystalline solar cells. Steel and iron sheet have been proposed as a substrate material for polycrystalline silicon solar cells.⁵ The ready availability and low cost of iron and steel sheet make them economically attractive as a structural support for large-area, terrestrial applications. However, low conversion efficiencies have been reported for polycrystalline silicon solar cells deposited on steel because of the incompatibility of the physical and metallurgical properties of silicon and steel.⁶ Metallurgical graphite has also been proposed as a substrate for silicon solar cells because of similarities in the coefficients of thermal expansion.⁷ For polycrystalline GaAs solar cells, Vohl et al. have recommended molybdenum and aluminum as metallic substrates.⁸ Aluminum has the advantage of exceptionally light weight, and excellent electrical properties, but a low melting temperature, whereas molybdenum has a volatile oxide which can be decomposed easily in the GaAs growth environment.

Multi-layered substrates have also been proposed for low-cost solar cells.⁸ In the simplest form, the multi-layered structure consists of a structural sub-layer and a conducting coating which compensates for disadvantageous properties of the sub-layer. In silicon solar cells,

diffusion barrier films of titanium, tungsten, molybdenum, silica and borosilicate glass have been proposed to prevent contamination of the semiconductor by impurities in the sub-layer.⁵ The possibility of utilizing multi-layer substrates expands the possible materials for the sub-layer to include insulators such as glass and ceramics, provided that the additional supported substrate film provides an electrical contact to the GaAs film, and aids in nucleation of GaAs.

Ideally, the substrate used for low-cost solar cells should be available in thin sheets at low or moderate cost and should not react with gaseous reactants or with GaAs under the conditions of the deposition. Also, the thermal expansion coefficient should match sufficiently with that of GaAs so as to avoid plastic deformation of the film during cooling from the film deposition temperature. The film obtained should have a strong adherence with the substrate and exhibit large grain size with columnar structure. Electrical properties of interest are high conductivity of the substrate and low ohmic contact resistance to GaAs, so that the metal can be utilized as one of the electric contact of the cell.

The properties of several metals potentially useful as substrates for GaAs solar cells are summarized in Table 1. Of the metals considered, nickel and iron-base alloys offer the lowest cost, but with the largest mismatch in the coefficient of thermal expansion. Tantalum matches the coefficient of thermal expansion of GaAs most closely, but has one of the highest costs of substrate metals. Molybdenum is available at a relatively low cost, but has a coefficient of thermal expansion which differs from that of GaAs by 14%.

Table 1. Properties of Substrate Materials

| Substrate Material | Thin Sheet* Price (cents/gr) | Price of a 0.2 mm* thick sheet \$/m ² | Melting temperature °C | Coefficient of Thermal Expansion (°C ⁻¹)×10 ⁶ |
|--------------------|---------------------------------|--|------------------------------|--|
| GaAs | > 100 | | 1238 | 6.4 |
| Ni | 1.3 | 23.1 | ~1453 | 13.0 |
| Stainless-Steel | 0.57 | 9.0 | 1535 (Fe) | 12 (Fe) |
| Ti | 2.1 | 18.9 | 1675 | 8.5 |
| Ta | 19 | 631 | 2996 | 6.5 |
| Mo | 6.8 | 138.7 | 2610 | 5 |
| W | 20.5 | 793.4 | 3410 | 4.5 |
| pyrex | 2.83 | 94.7 (1/16" thick sheet) | | 3.3 |
| graphite | | | > 3350 | variable |

*From Ref. 9.

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D. Experimental

GaAs films were prepared from trimethyl gallium (TMG) and arsine in a hydrogen carrier gas, in an rf-heated reactor. The experimental apparatus and procedure used to fabricate thin films of GaAs are described in Chapter III.

Materials used were metallurgical grade metals and graphite (99.9% purity) and ordinary pyrex glass. Prior to the deposition, the samples were degreased in hot solvents, and metallic substrates were etched for 10 min. in hot hydrochloric acid. GaAs films were then deposited on each substrate under conditions optimized from growth on single-crystal GaAs. The growth conditions were 1 l/min H_2 , $0.41 \text{ cm}^3/\text{min}$ TMG, $12 \text{ cm}^3/\text{min}$ AsH_3 , a substrate temperature of 750°C , and a deposition time of 10 min.

To evaluate the interface resistance, a gold probe 0.5 mm diameter was placed on the top surface of the GaAs film and a contact was established with the substrate. A current through the resulting diode was then increased until breakdown occurred. Then, the total resistance of the diode was measured using a I-V curve tracer.

The resistance measured is the sum of the following resistances:

- (a) resistance of the wires
- (b) resistance of the Au/GaAs interface
- (c) resistance of the GaAs layer.
- (d) resistance of the GaAs/metal interface
- (e) resistance of the metal

The terms (a) and (e) are negligibled with the wires used. The carrier concentration of the samples is about 10^{16} cm^{-3} , and the thickness of the film of GaAs is only a few microns so term (c) is also negligible. The term (b) is assumed to be very small when the breakdown of the diode has occurred, or at least to be about constant in all experiments. Thus, the measured resistance is a good approximation for the resistance of the GaAs/metal interface.

E. Results and Discussion

A number of metals were found to react with arsenic under the conditions of the deposition. In the films obtained, some compounds were identified by X-ray diffraction analysis and are reported in Table 2.

Experimental films of GaAs on Ta, Mo, W, graphite and pyrex were also studied. A scanning electron micrograph of a 3-5 μm thick deposited film of GaAs is shown in Fig. 1. Interfacial properties are given in Table 2.

Nickel appears to have the desired electrical properties since it has been used to make ohmic contact with GaAs. However, under the conditions of the deposition, nickel was found to react with arsenic, as NiAs and other compounds of As and Ni were identified in the film.

Stainless steel and Ti were also found to react with arsenic, although some films of GaAs were successfully deposited on these metals without the formation of interfacial reaction products. Because of the reaction products found, however, these metals were rejected as optimal substrates.

Table 2. Properties of the GaAs Substrate Interface

| Substrate Material | Interfacial resistance (Ω) | Interfacial Reaction Product Phases |
|--------------------|-------------------------------------|--|
| Ni | low | NiAs, $(\text{Ni}_5\text{As}_2)\text{H}$ |
| stainless steel | low | FeAs, FeAs_2 , |
| Ti | 0.35 | $(\text{Ti}_5\text{Ga}_4)_8\text{H}$ |
| Ta | 1.80 | |
| Mo | 0.52 | MoAs_2 at high temperature |
| W | 0.92 | |

The surface morphologies of GaAs films deposited on various substrates are shown in the scanning electron micrographs of Fig. 1. The grain size on all substrates was distributed, indicating that new crystallites were continuously nucleated during the growth process.

Large grains were obtained on tungsten substrate, but these were separated by voids. Such films would exhibit a very low shunt resistance when the junction is formed. Thus this metal was not considered to be suitable as a substrate for thin-layer GaAs solar cells.

Tantalum was rejected on the basis of its very high cost, as shown in Table 1 and of its high interfacial contact resistance with GaAs as shown in Table 2.

Of the remaining substrate materials, Mo, glass and graphite, graphite appears to give the largest grain size and thus was selected for further study. Also, molybdenum was found to exhibit a favorable combination of properties: the GaAs layer adheres well to this metal without forming interfacial reaction products, the thermal expansion is close to that of GaAs, and the cost is relatively low. This metal was also selected for further study in spite of its relatively high contact resistance to GaAs.

F. Conclusion

The properties of several materials potentially useful as substrates for solar cells have been compared. Stainless steel, Ni, Ti are unsuitable because they react with As under the conditions of GaAs deposition.

Among the potential substrate materials, graphite and Mo appear to have adequate physical and electrical properties.

FIGURE CAPTION

Fig. 1. Scanning electron micrographs of GaAs films deposited on different materials: (a) stainless steel, (b) tantalum, (c) molybdenum, (d) tungsten, (e) pyrex and (f) graphite.

Growth conditions were:

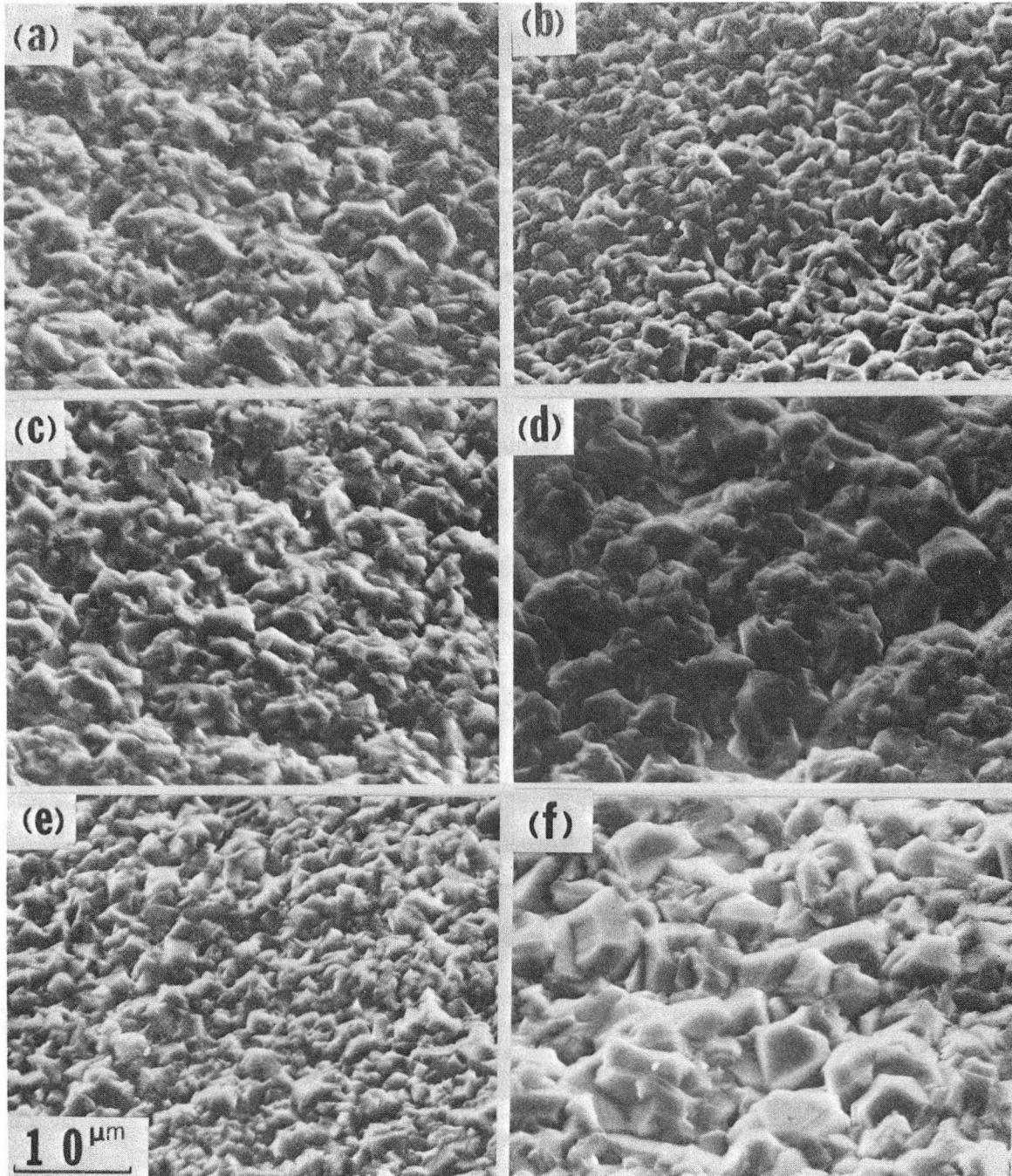
temperature: 750°C

hydrogen flow rate: 1 l/min.

TMG concentration: 0.041%

As/Ga = 29

Growth time: 10 min.



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Fig. 1

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III. PROPERTIES OF CHEMICALLY VAPOR DEPOSITED FILMS OF GaAs ON GRAPHITE

A. Abstract

Toward the realization of cost-effective GaAs solar cells for terrestrial application, polycrystalline GaAs films have been deposited on graphite by chemical vapor deposition using trimethyl gallium and arsine in a hydrogen carrier gas.

The effects of growth conditions such as the substrate temperature and reactant concentrations and of substrate surface preparation by mechanical polishing and sand blasting on growth rates and microstructure have been studied using optical and scanning electron microscopy and by X-ray diffraction analysis. Electrical properties of the films are also presented.

B. Introduction

GaAs is one of the most promising compounds for the preparation of solar cells. This compound semiconductor exhibits a favorable band gap for maximum conversion efficiency of the solar spectrum and the lowest dependence of electrical performances upon temperature. The preparation of single crystal GaAs solar cells has already been reported^{1,2,3} but, these remain economically unattractive for terrestrial applications because of the high cost of the GaAs substrates required if used without concentrators or to the cost of the concentrators. The absorption coefficient of GaAs is sufficiently high that

a thin layer of 3-5 μm in thickness is sufficient to absorb the majority of the energy contained in the solar spectrum. A cell consisting of such a thin film deposited on a low-cost foreign substrate would be much more attractive economically because of the much lower amount of gallium needed, provided that the performances of the cell are not degraded significantly by the polycrystallinity of the film.

The effect of grain boundaries on the performances of a polycrystalline cell have been recently discussed and calculated.⁴ Due to the low diffusion length of minority carriers in GaAs, a fabrication technology capable of producing films with columnar grains of a few microns diameter and of height equal or smaller than the diameter would result in an photovoltaic energy conversion efficiency close to the maximum possible.

The preparation of GaAs films by chemical vapor deposition using the system $\text{Ga}(\text{CH}_3)_3/\text{AsH}_3/\text{H}_2$ is, to date, the most attractive method of producing GaAs films for terrestrial solar cells applications.⁵ In an attempt to produce films having the required mechanical and electrical properties, GaAs has been deposited on metallurgical grade graphite by this method. Graphite has been selected for the film substrate on the basis of its low cost and high electrical conductivity. This substrate material can also be used as one of the electrical contacts of the cell. The influence of growth conditions such as substrate temperature and concentrations of reactants on the microstructure of the film has been studied using X-ray diffraction technique and optical and scanning electron microscopy. The graphite substrate

surfaces were prepared by industrial polishing, by mechanical lapping, and by sand blasting in order to examine the effect of surface preparation on film defect density and on film microstructure. Finally, electrical properties of the resulting films are presented.

C. Experimental

1. Apparatus

The apparatus used for the deposition of GaAs is shown schematically in Fig. 1. The concentrations of reagents in the carrier gas were regulated by flow metering valves. The trimethyl gallium (TMG) was contained in a cylindrical pyrex and stainless steel saturator maintained at 0°C, through which hydrogen was sparged to vaporize the TMG. The gases are thoroughly mixed before entry into a water-cooled, vertical quartz reactor 4 cm in diameter and 30 cm in height. Samples were placed on a graphite susceptor at the top of a quartz pedestal and are heated by RF coil, whereas the reactor is cooled to create a cold wall and avoid undesired deposition of GaAs. Temperature, measured by a thermocouple was corrected by an appropriate calibration to compensate the effects of the rf current in the thermocouple.

2. Reactants

The reactants used in preparing the GaAs layers were 99.9% trimethylgallium (Ventron corporation) and 99.995% arsine (Matheson Gas Products). The hydrogen carrier gas was purified by passing over a Deoxo catalyst to remove oxygen, then by diffusion through palladium. Helium was used with no special purification as a purge gas. Substrates

were prepared from 99.9% pure graphite with a density of 1.75 g/cm^3 (Union Carbide). Typical substrates are 12 mm square and 5 mm thick.

3. Procedure

The samples were prepared by chemical cleaning and by mechanical methods in order to compare the effect of surface preparation methods. Samples selected to minimize the density of surface defects and scratches were used in the unpolished condition. Mechanically polished samples were prepared by polishing to a $1 \mu\text{m}$ finish. Sand blasted samples were prepared by sand blasting with $20 \mu\text{m}$ silicon carbide abrasive for a period of 10 s/cm^2 .

All samples were chemically degreased by boiling for 10 min. each in perchloroethylene, acetone, methanol and isopropyl alcohol, then stored for subsequent use in a dust-free container. Immediately before introduction into the reactor, the substrates were cleaned again with dichlorodifluoromethane gas to remove any dust particles from the surface. To minimize contamination from the susceptor, the graphite susceptor was given the same cleaning treatment.

Chemical vapor deposition of GaAs from trimethylgallium and arsine was carried out as follows. After the graphite substrate and susceptor were placed within the reactor, helium was allowed to flow for a period of 5 min. in order to remove all air from the system. Then hydrogen was allowed to flow for an additional 10 min. period to displace all helium. The substrate was then heated to about 1000°C for 10 min. in hydrogen in order to desorb unwanted gases from the substrate surface. The temperature was then reduced to the growth temperature and the flow

of arsine begun. The flow of hydrogen through the trimethyl gallium saturator was then begun.

Following the growth period the trimethyl gallium flow was stopped, and the sample temperature reduced rapidly to approximately 350°C. Then the flow of arsine was turned off, and the sample allowed to cool to room temperature. The reactor was purged with helium before the sample was removed.

4. Film Characterization

Growth rates of GaAs on all substrates was observed to be homogeneous across the substrate, except at edges where there was a lower film density and sometimes dendritic growth. All properties were measured in the vicinity of the center of the samples where the highest growth homogeneity was found.

Films were characterized using X-ray diffraction with $\text{CuK}\alpha$ X-ray source, and film surfaces examined by optical and scanning electron microscopy. Vertical cross sections were prepared by cutting the sample, polishing to a 1 μm diamond finish and etching with 1% by volume of bromine in methanol.

Growth rates were determined from the film thickness measured on the vertical cross section and from the deposition time. For most of the films deposited, the void fraction was very small, and thus the measured growth rates were very close to the true growth rates.

Concentrations of TMG were calculated based on the assumption that thermodynamic equilibrium at 0°C is reached in the bubbler containing TMG and that this equilibrium can be described by Roault's law.

Doping level of the films was deduced from voltage breakdown measurements (without correction for the grain boundaries). Carrier type was determined by the hot-cold probe technique and by observation of the electrical characteristics of Schottky barrier cells.

D. Results

1. Film Microstructure

GaAs films with thicknesses between 5 and 50 μm were deposited under different conditions of growth. The films were all found to be polycrystalline with grain size decreasing with increasing film thickness. The cross section of a 20 μm thick GaAs film on unpolished graphite is shown in Fig. 2. It can be seen that larger crystallites are found close to the top surface but no columnar structure was obtained in the normal direction. Similar examinations of films grown on substrates containing surface defects showed that the substrate defects are replicated in the GaAs film, and some major mechanical defects such as pits and hillock generate a high density of grain boundaries. Crystallites found at the top of thin layers (3-6 μm thick) are typically 2-5 μm in diameter with some variation in the grain size. X-ray diffraction analysis shows that the films were randomly oriented with a (422) preferred orientation with respect to the substrate plane.

2. Effect of Growth Conditions

The growth conditions were found to have an influence on the growth rate and on the mechanism of growth. Therefore, the growth conditions have a strong influence on the properties of the deposited layers.

Higher concentrations of TMG were found to produce higher growth rate as expected. Surprisingly, larger crystallites were obtained at higher growth rates, up to a maximum size of about $5 \mu\text{m}$ at TMG molar concentrations greater than 0.6×10^{-3} , as shown in Fig. 3.

Measured growth rates are shown as a function of TMG concentration in Fig. 4 and compared with growth rates observed for (100) GaAs single crystal substrates grown in the same reactor.⁶ At low TMG concentrations, the rates are lower than the growth rates on (100) GaAs. At higher concentration, the rates are much larger and depend also on the defect density of the substrate. As will be discussed below, the nucleation of GaAs is critically dependent on the nature of the surface and on surface preparation. The growth rate on unpolished samples exhibited differences in growth rates under the same experimental conditions, depending on the defect density in the substrate surface.

These observations tend to show that the nucleation rate is less dependent on TMG concentration than the growth rate. This effect accounts for the larger crystallites at the higher concentration of TMG. The low deposition rates obtained at low concentrations are due to the process of incubating nuclei having critical size to start crystal on the relatively flat and edge-free graphite surface. In the vicinity of mechanically induced surface defects, however, the smaller crystallites obtained indicate that a higher nucleation rate is present in such region. When the graphite surface is completely covered with GaAs much higher density of sharp edges allows growth to occur more easily, thus leading to the high observed growth rates.

The effect of substrate temperature on the morphology of GaAs crystallites is shown in Fig. 5. At temperatures near 600°C, only dendrites were formed, as shown in Fig. 5a. At lower temperature, the deposition rate diminishes as a consequence of the surface reaction-controlled growth. Between 700°C and 960°C, relatively uniform films were obtained, with crystallite size increasing with temperature, as shown in Figs. 5b-e. In this range, the growth is most probably limited by the diffusion of reactants through a momentum boundary layer adjacent to the surface. At temperatures above 1000°C, dendritic growth occurred in competition with isotropic growth, as shown in Fig. 7f. At low temperatures the rate of nucleation is expected to be high and critical size clusters are more likely to form, thus leading to a small grain size. At higher temperatures, the nucleation rate is reduced by enhanced desorption, and thus larger crystals are obtained.

The mechanisms for growth in different temperature ranges are summarized in Fig. 6. At temperatures below 680°C, and above 960°C, dendritic growth predominates. Surface reaction controlled growth appears to prevail between 680°C and 750°C, while diffusion controlled growth dominates between 750°C and 960°C, and the growth rate is nearly independent of temperature. The diffusion controlled growth regime spans a wider temperature range than the corresponding growth on (100) GaAs, shown by the dotted line in Fig. 6, as reported by Lin and Donaghey.⁶

3. Effect of Surface Preparation

The surface of the unpolished form of the high density graphite studied, although macroscopically flat and free of gross defects, did exhibit mechanical defects such as: scratch, hillocks and pits which

increased the local defect density in the grown GaAs film, as shown in Figs. 7a-b. Thus, the grown films had an appreciable defect density at their outer surface.

In an attempt to reduce the defect density in the graphite substrate surface before chemical vapor deposition, mechanical polishing to a 1 μm diamond finish was carried out. This surface treatment is a simple way to obtain a flat surface, but as an industrial operation, it is very costly. A second method of surface preparation studied was sand blasting which is a much cheaper industrial operation for reducing surface defects.

A comparison of graphite surfaces before and after deposition for unpolished, mechanically polished and sand blasted graphite substrates is shown in Fig. 7, for growth at 750°C with molar flows of 7.44×10^{-4} , 3.0×10^{-7} and 8.9×10^{-6} mole/s of H_2 , TMG and arsine, respectively. Mechanical polishing removes scratches and hillocks which are found at the surface of graphite, but creates a large number of holes due to the presence of many pores in the bulk graphite. The deposition of GaAs on mechanically polished graphite produces a layer with fewer hillocks, and an increased number of voids, but the size of crystallites is essentially the same, as shown in Fig. 7(c) and (g). The deposition rate is about 25% lower on mechanically polished graphite as compared to that on unpolished graphite. This effect is probably due to the flatter surface of the mechanically polished sample as shown in Figs. 7a-e so that nucleation is more difficult than on the unpolished surface.

Sand blasted graphite has a rough, mountain-like surface with many defects (Fig. 7i). Growth is not uniform, but takes the form of small spheres (Figs. 7j-1). This effect might be due to the presence of

inhibiting defects of a similar nature in the substrate surface.

4. Electrical Properties

Without intentional doping the GaAs films grown were usually n-type and had carrier concentration of about $5 \times 10^{16} \text{ cm}^{-3}$. These are mostly due to the impurities contained in graphite which diffused into the GaAs film during growth, and to the high As/Ga ratio used during the growth. As expected, at high temperature or at low growth rates, the carrier concentration increased, up to about 10^{17} cm^{-3} , and p-type conductivity was found in some GaAs films grown.

Attempts were made to prepare Schottky barrier solar cells using 5 μm thick layers of GaAs grown at 750°C. However, the cells made had always very low short circuit current and very high series resistance because of the high resistance of the interface graphite/GaAs.

E. Conclusions

In an attempt to prepare films of GaAs having adequate properties for thin film solar cells for terrestrial application, GaAs has been deposited by CVD using the system $\text{Ga}(\text{CH}_3)_3/\text{AsH}_3/\text{H}_2$ on metallurgical grade graphite, and the properties of the films obtained studied with respect to growth conditions (temperature, concentration of reactants) and surface preparation (mechanical polishing, sand blasting).

Films obtained are polycrystalline, randomly oriented, with grain size of 1 to 5 μm depending on the growth conditions. Higher temperatures (up to 960°C) and larger input of TMG mole fractions produce larger grain size. Deposition rates are nearly proportional to the TMG mole fraction and independent of temperature in the range $750 < T < 960^\circ\text{C}$.

Mechanical polishing of the graphite reduces the defect density but introduces holes in the GaAs films because of the porosity of graphite; and sand blasting the graphite produces a roughened GaAs layer.

Schottky barrier solar cells have been prepared using the films grown but they always exhibited a very low short circuit current and a very high series resistance because of the high resistance of the interface graphite/GaAs.

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FIGURE CAPTIONS

- Fig. 1. Experimental apparatus for the chemical vapor deposition of GaAs.
- Fig. 2. Vertical cross section of a GaAs layer deposited on graphite.
- Fig. 3. Scanning electron micrograph of GaAs deposited on unpolished graphite at 750°C, a hydrogen flow rate of 7.44×10^{-4} moles/s (1 l/min) and As/Ga = 24 for different TMG mole fractions and growth time:
- | | |
|---------------------|-----------------------|
| (a) 0.015%; 30 min. | (b) 0.024%; 21.5 min. |
| (c) 0.041%, 10 min. | (d) 0.062%, 10 min. |
| (e) 0.11%; 10 min. | (f) 0.17%; 10.5 min. |
- Fig. 4. Growth rate at 750°C as a function of TMG mole fraction.
- Fig. 5. Scanning electron micrographs of GaAs deposited on unpolished graphite at different temperatures, for a hydrogen flow rate of 7.44×10^{-4} mole/s (1 l/min.), $\text{AsH}_3/\text{TMG} = 24$ and a growth time of 10 min. (11 min for sample a): a) 600°C, b) 700°C, c) 800°C, d) 900°C, e) 960°C, f) 1000°C.
- Fig. 6. Effect of substrate temperature on the growth rate of GaAs on unpolished graphite.

Fig. 7. Comparison of substrates and GaAs films deposited on (first row) unpolished, (second row) mechanically polished, and (third row) sandblasted graphite. First column: SEM micrograph of substrate surfaces before deposition. Second and third columns: GaAs films at different magnifications. Fourth column: vertical cross sections of deposited GaAs layers. Growth conditions: substrate temperature, 750°C; H₂ flow rate 7.44×10^{-4} mole/s (1 l/min); TMG mole fraction, 0.041%; As/Ga molar ratio, 30; deposition time, 40 min.

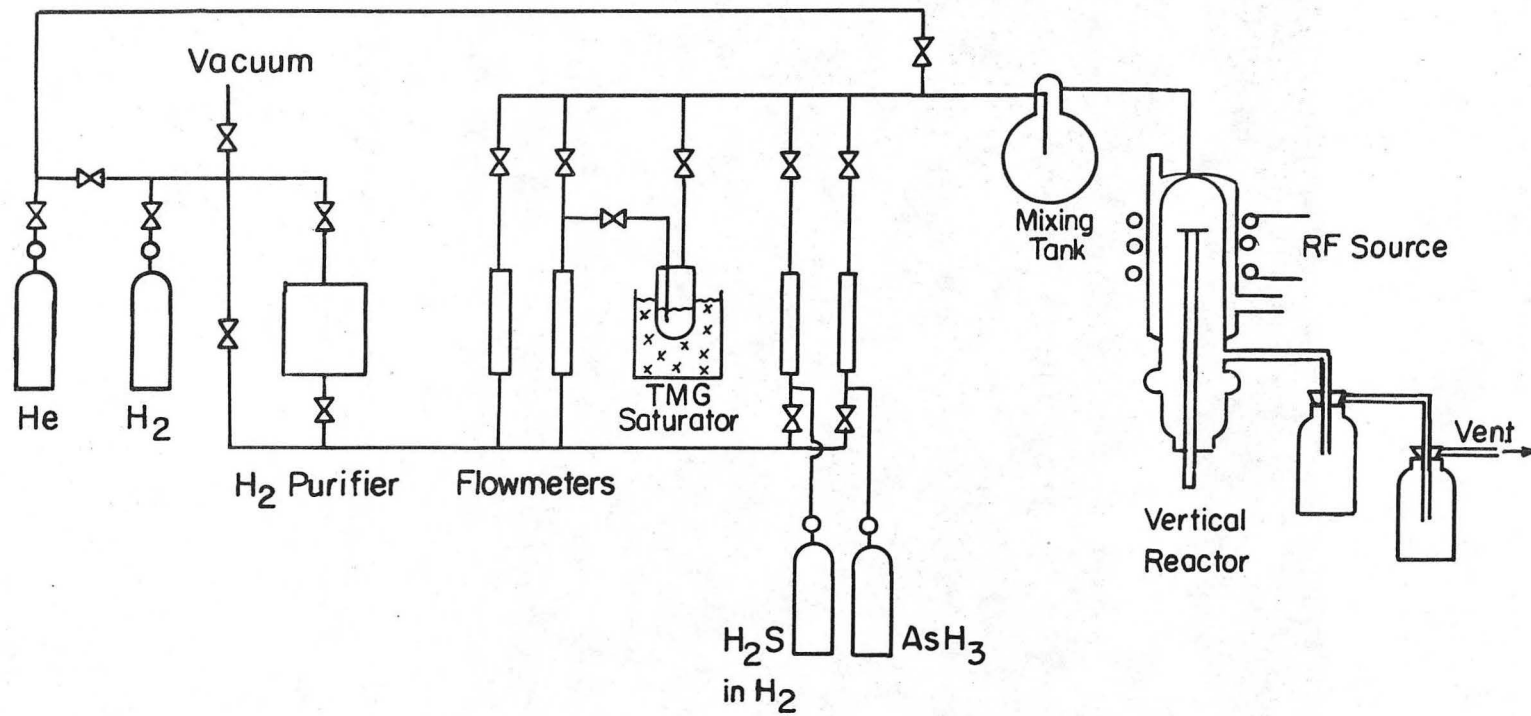
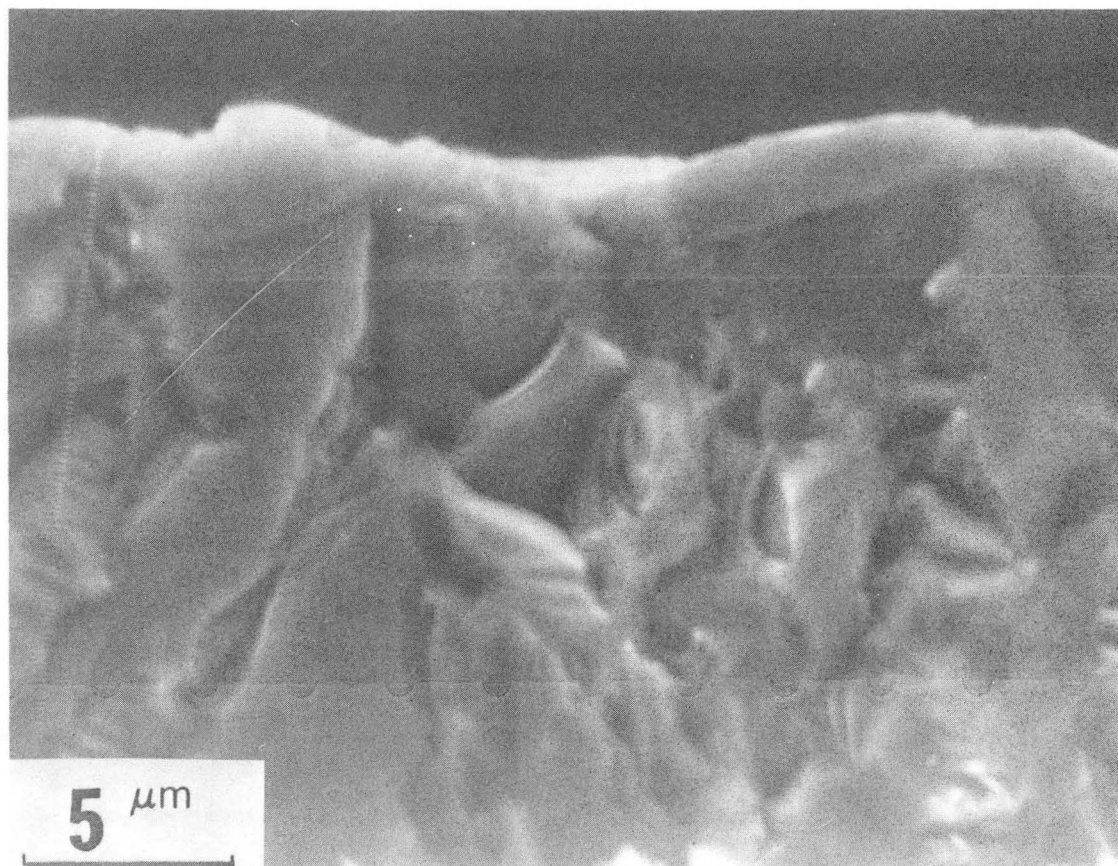


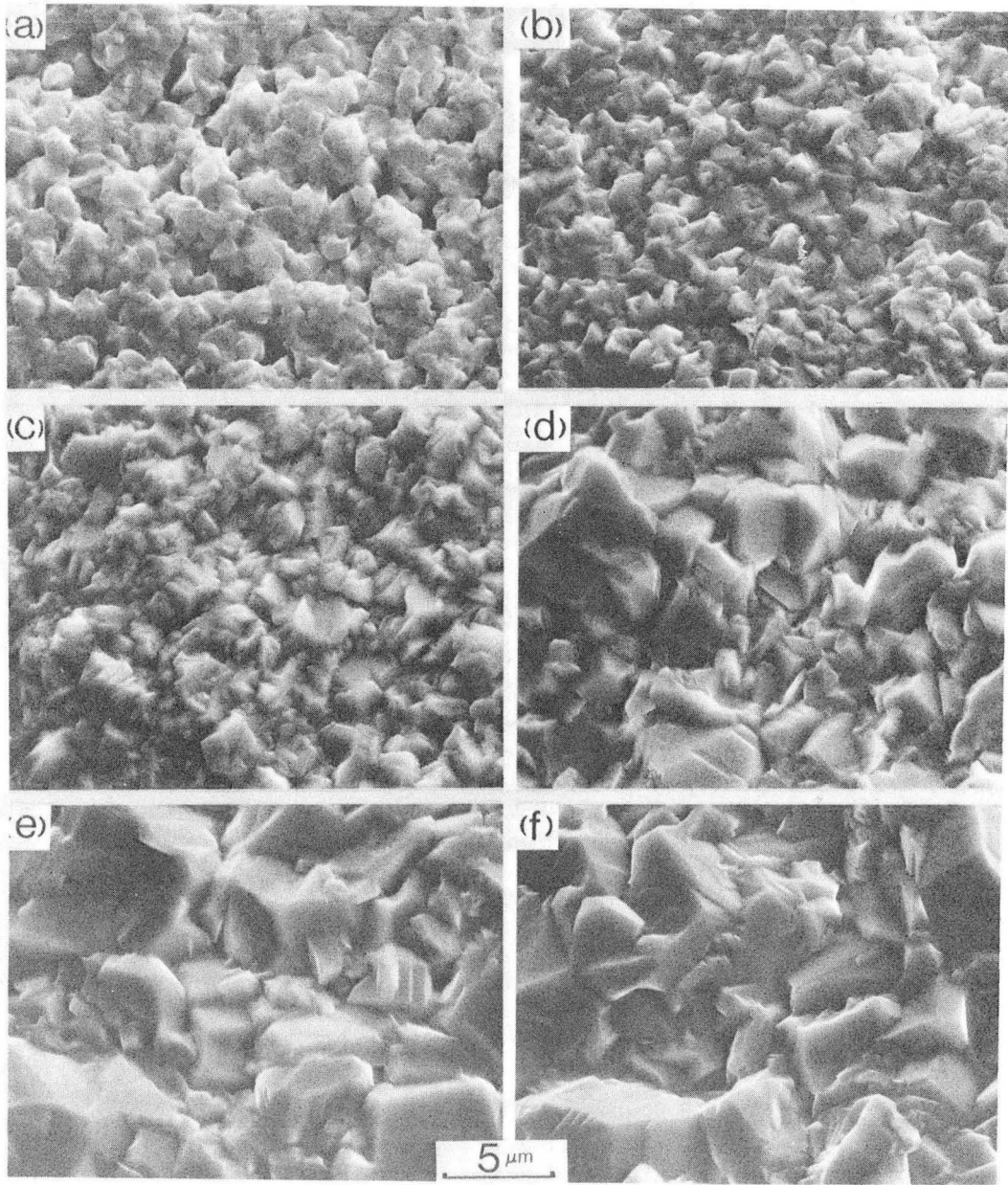
Fig. 1.

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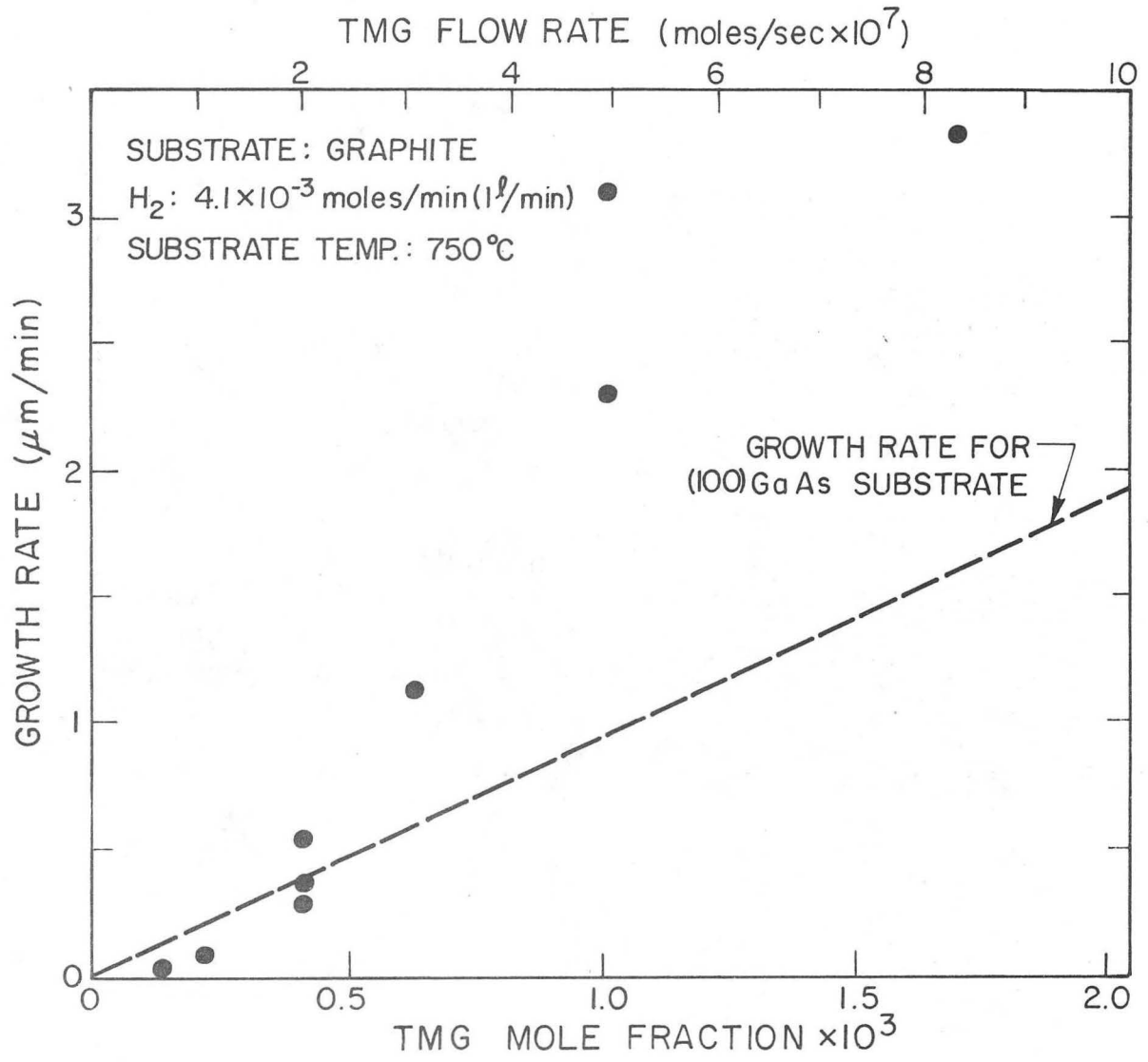
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Fig. 2.



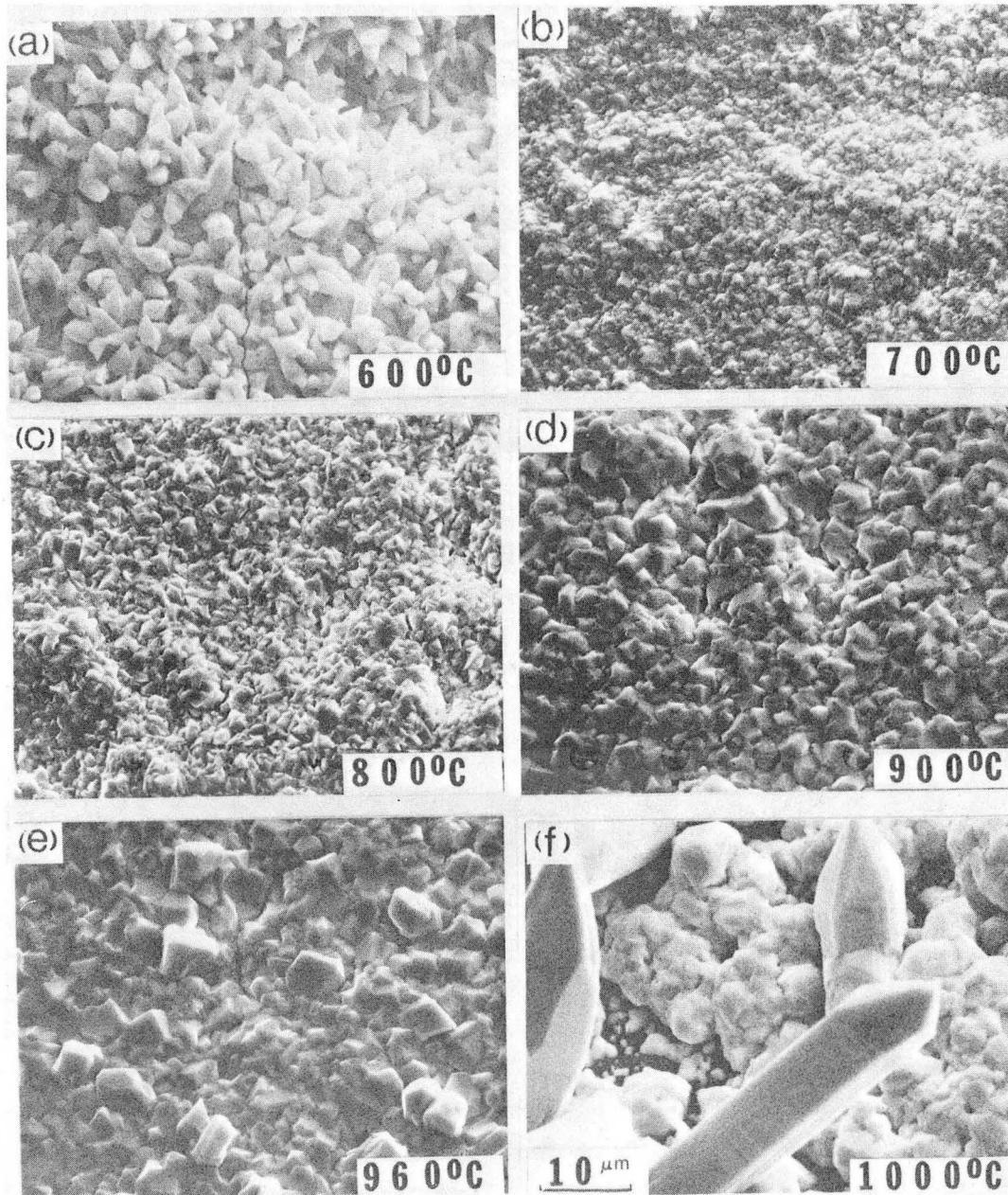
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Fig. 3.



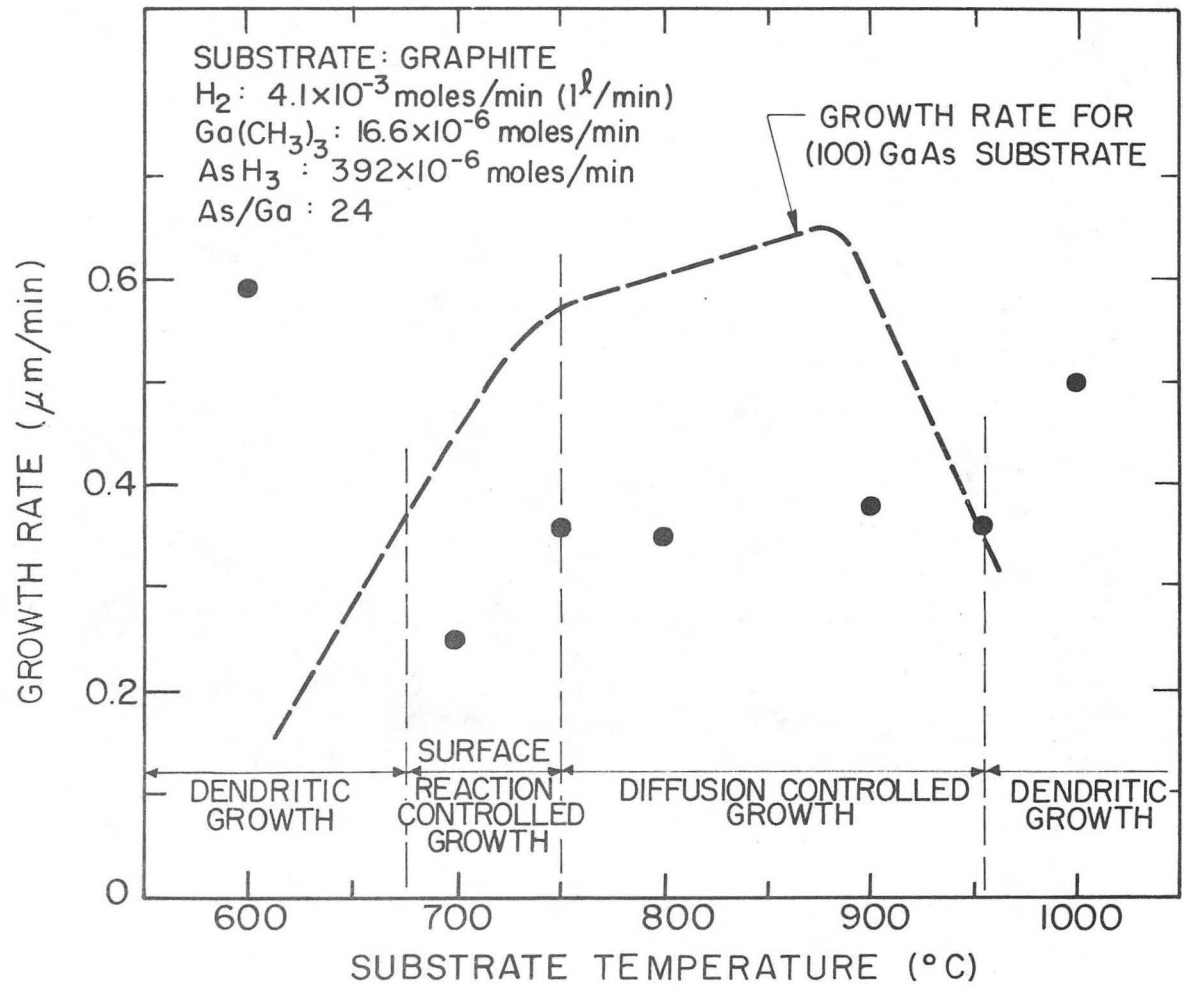
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Fig. 4.



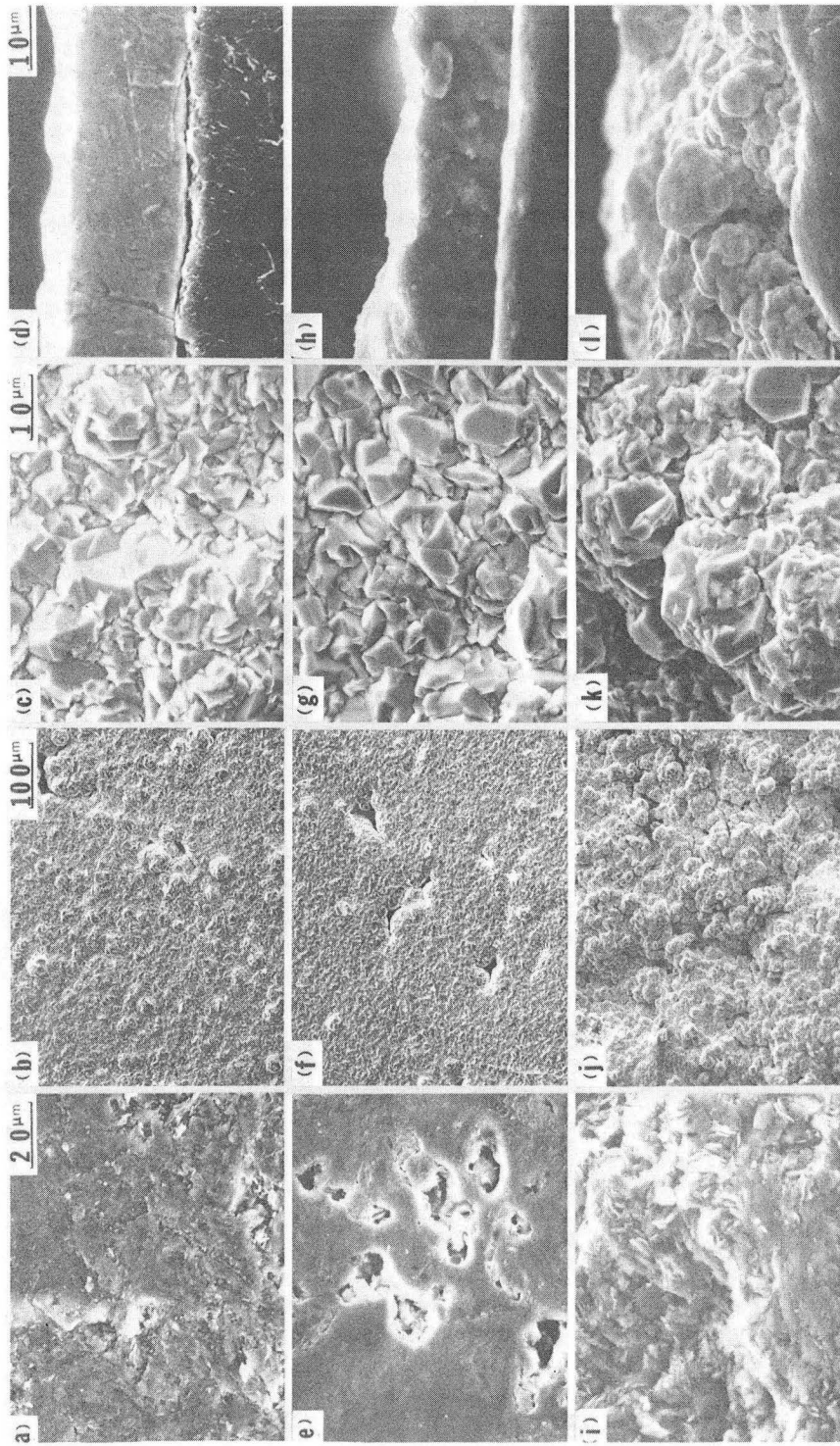
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Fig. 5



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Fig. 6.



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Fig. 7.

IV. CHEMICAL VAPOR DEPOSITION AND PROPERTIES OF GaAs ON MOLYBDENUM SUBSTRATES

A. Abstract

Toward the realisation of cost effective solar cells for terrestrial application, GaAs has been deposited on metallurgical grade molybdenum by chemical vapor deposition using trimethylgallium (TMG) and arsine in a hydrogen carrier gas.

The influence of the substrate temperature, TMG mole fraction, AsH_3/TMG molar ratio and H_2S mole fraction on the microstructural properties of the deposited layers have been studied using X-ray diffraction and scanning electron microscopy. Electrical properties of the layers are also reported.

B. 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 GaAs¹ 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 μm thick is sufficient to absorb most of the solar spectrum with energy in excess of the band gap.² Also, it has been shown recently that a GaAs grain size in the range of 3-5 μm would be sufficient to attain 90% of the maximum conversion efficiency.³

A recent review of potential, low-cost substrates for GaAs solar cells has shown that molybdenum has several advantages over other metals.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.⁵

The object 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 $\text{Ga}(\text{CH}_3)_3$ (TMG)/ AsH_3/H_2 is described.

To date, this method of preparation appears to be most attractive for the large scale fabrication of solar cells.²

C. 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, 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 perchloroethylene, acetone, methanol and isopropyl alcohol. Samples were then chemically polished in a 6:2:1 mixture of lactic:nitric:hydrofluoric acids.⁶ Immediately before the deposition, a final cleaning with a dichloro-difluoromethane 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 flowrate of 1 liter/min was used in experimental runs.

At the end of helium and hydrogen purge periods, the sample and susceptor were annealed at about 1000°C for 10 min. in hydrogen to reduce possible oxides at the surface of 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 H₂S 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 H₂-TMG equilibrium. The vapor pressure of TMG at 0°C was taken from the literature to be 8.60 kPa (64.5 Torr).

D. Results

The chemically vapor deposited GaAs films were studied to determine the effect of growth conditions, such as substrate temperature, reactant mole fractions and H₂S 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 μm, while in other experiments film with thickness between 10 and 30 μm 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 μm, 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 μm diamond paste, and etched in a solution of 1% bromine in methanol. A scanning electron micrograph of the cross section of a 30 μm GaAs layer deposited at 800°C with the TMG mole fraction, $y_{\text{TMG}} = 0.0017$, and arsenic to gallium input ratio, $\text{As/Ga} = 24$ 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 μm. With increasing distance from the substrate, the grain

size increases, so that at the top surface of the film, grains larger than $4 \mu\text{m}$ 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 $5 \mu\text{m}$ 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 $1 \mu\text{m}$ at 600°C to up to $5 \mu\text{m}$ 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 MoAs_2 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 $700^\circ\text{C} < T < 875^\circ\text{C}$.

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 $y_{\text{TMG}} \approx 0.001$. 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.⁷ 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 6×10^{-3}) are less than the growth rates on (100) GaAs, whereas at much higher TMG mole fraction, the growth rates are higher on Mo.

It has been shown in a previous work⁸ 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 $\text{Ga}(\text{CH}_3)_3$, 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_2S dopant. Variations in the microstructure of the molybdenum substrate also appears to influence the critical As/Ga ratio required for dendritic growth.

Effect of H₂S Dopant

Undoped GaAs samples were found to be n-type with a carrier concentration of about $5 \times 10^{16} \text{ cm}^{-3}$. 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 H₂S 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 H₂S, the carrier concentrations were found to vary linearly on a log-log scale with the concentration of H₂S over several orders of magnitude. These results show that doping level in the GaAs film can be controllably set.

The introduction of H₂S during the growth process was found to have no significant influence on the morphological properties of the films, for H₂S mole fractions up to 2×10^{-4} . This mole fraction was an order of magnitude larger than the maximum mole fraction of H₂Se (about 3×10^{-5}) which could be introduced under similar growth conditions without affecting the microstructure of the GaAs films.⁹

E. Conclusions

Polycrystalline GaAs layers have been deposited on polycrystalline molybdenum sheet by pyrolysis of $\text{Ga}(\text{CH}_3)_3$ and AsH_3 , for application to terrestrial solar cells. Characteristics of the growth process and 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 4 μm .

Higher temperatures up to 875°C produced larger GaAs crystallites. At higher temperature (above 950°C), molybdenum and arsenic were found to react to form MoAs_2 in the substrate.

Larger input concentrations of TMG produced larger GaAs crystallites but also a more roughened surface of the deposited film. At lower 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 higher 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 H_2S 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 H_2S are n-type, and the carrier concentration varies linearly with the partial pressure of H_2S on a log-log scale.

Table 1. Comparison of GaAs Deposition Rates on Mo and (100) GaAs at 800°C.*

| Input Ga(CH ₃) ₃ mole fraction × 10 ³ | Deposition Rate, μm/s(μm/min) | |
|---|-------------------------------|----------------------|
| | Mo Substrate | (100) GaAs Substrate |
| 0.41 | 0.0042(0.25) | 0.0068(0.41) |
| 0.87 | 0.0223(1.34) | 0.0145(0.87) |
| 1.72 | 0.0633(3.80) | 0.0290(1.74) |

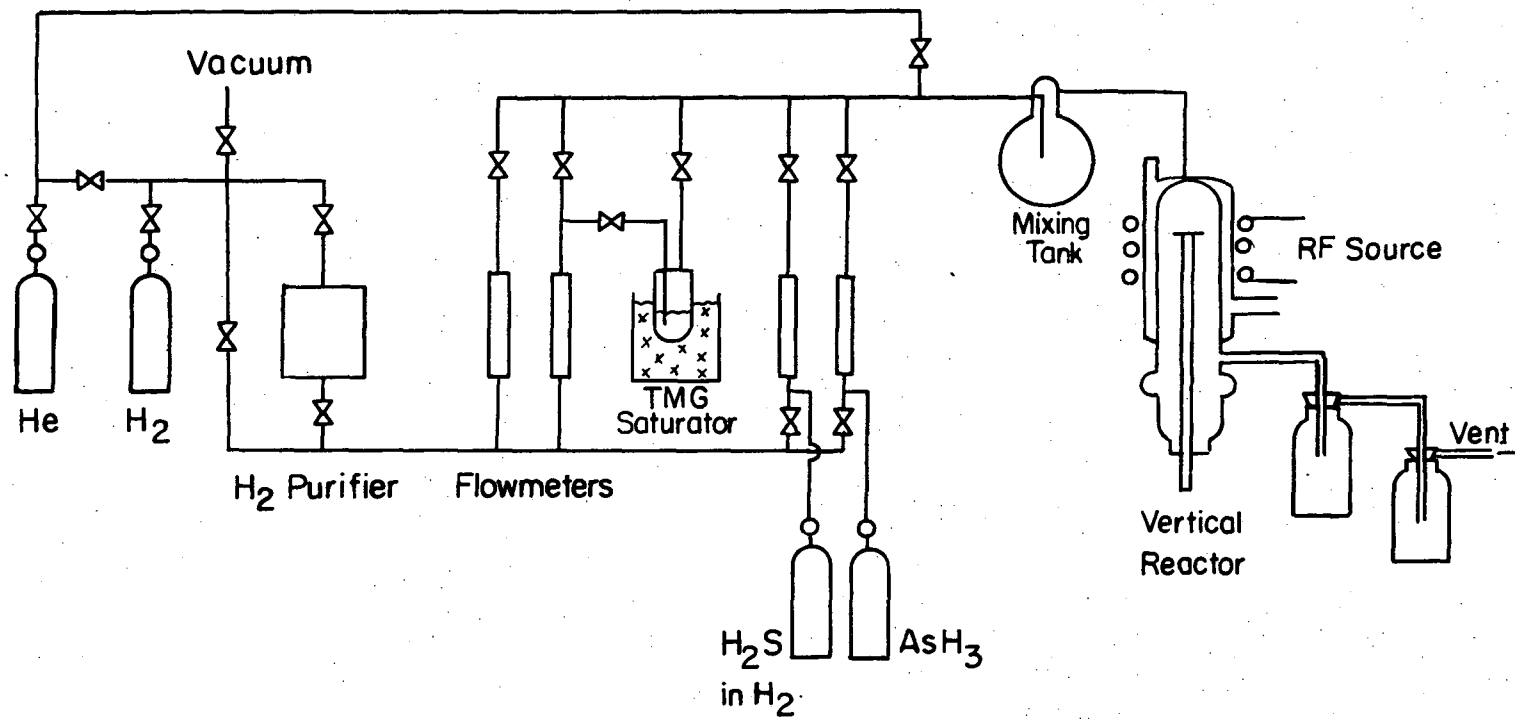
* Experimental conditions:

H₂ flow rate: 16.7 cm³/s (1 l/min)

AsH₃/Ga(CH₃)₃ ratio = 24

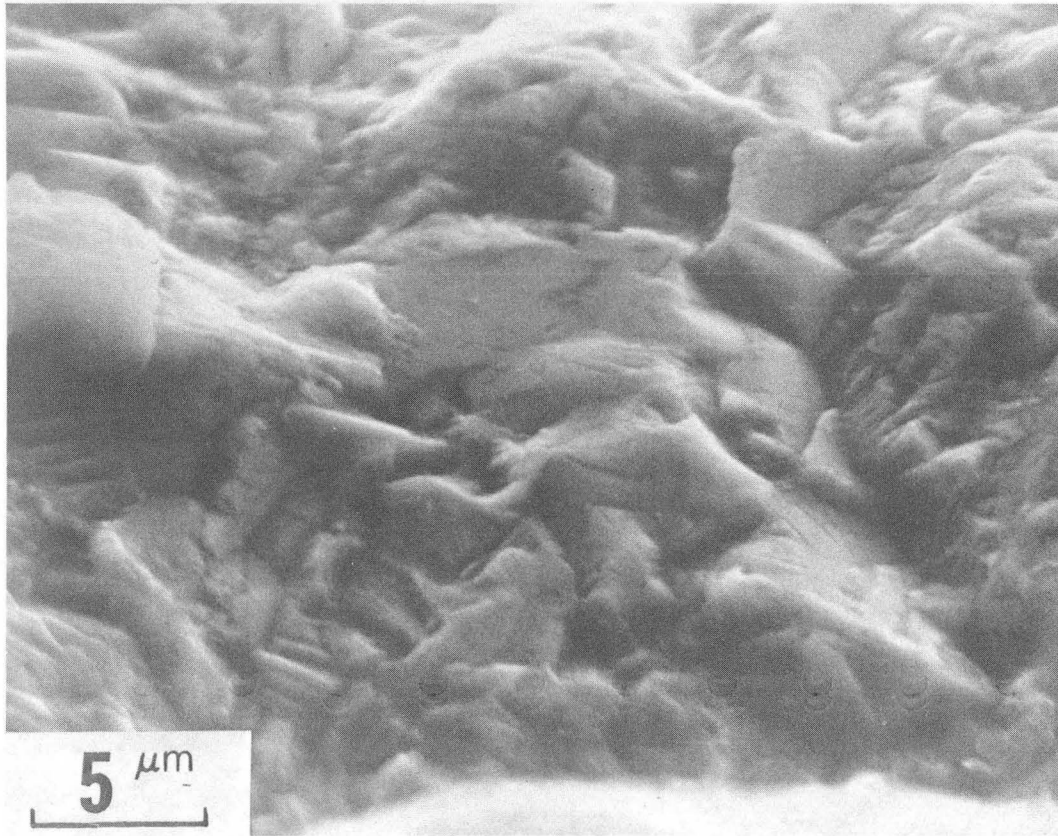
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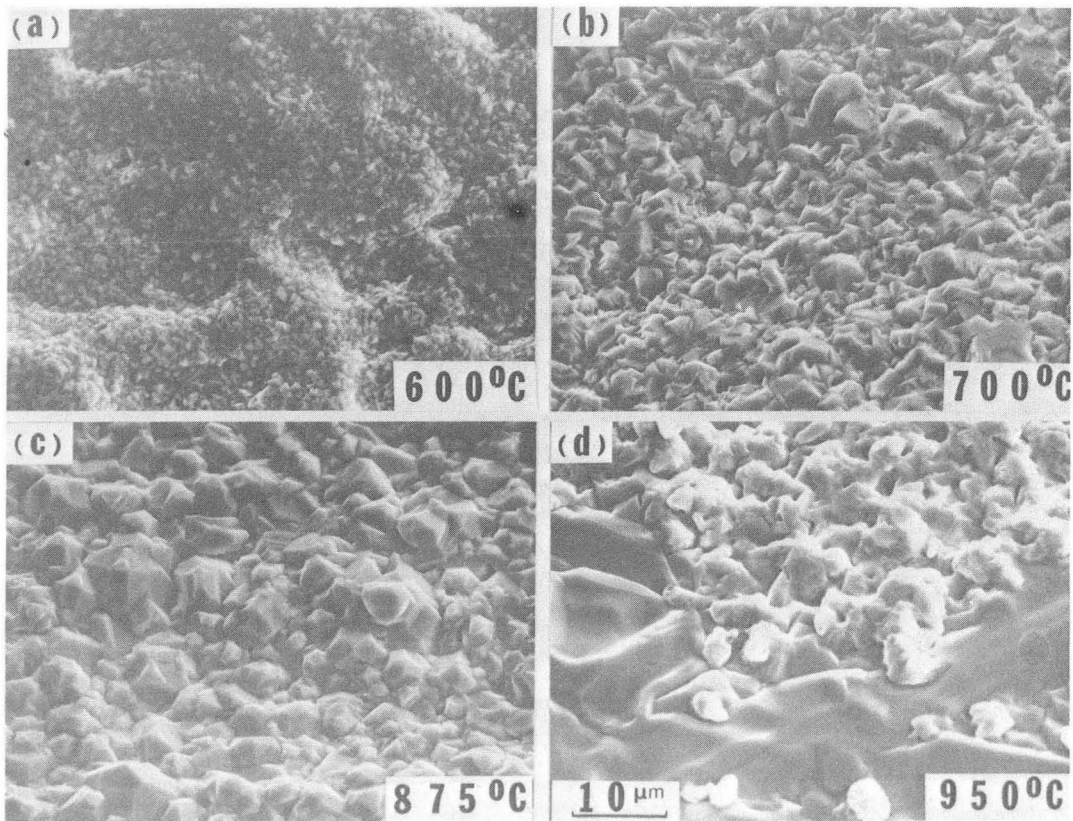
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Fig. 1. Schematic diagram of the apparatus for chemical vapor deposition of GaAs.



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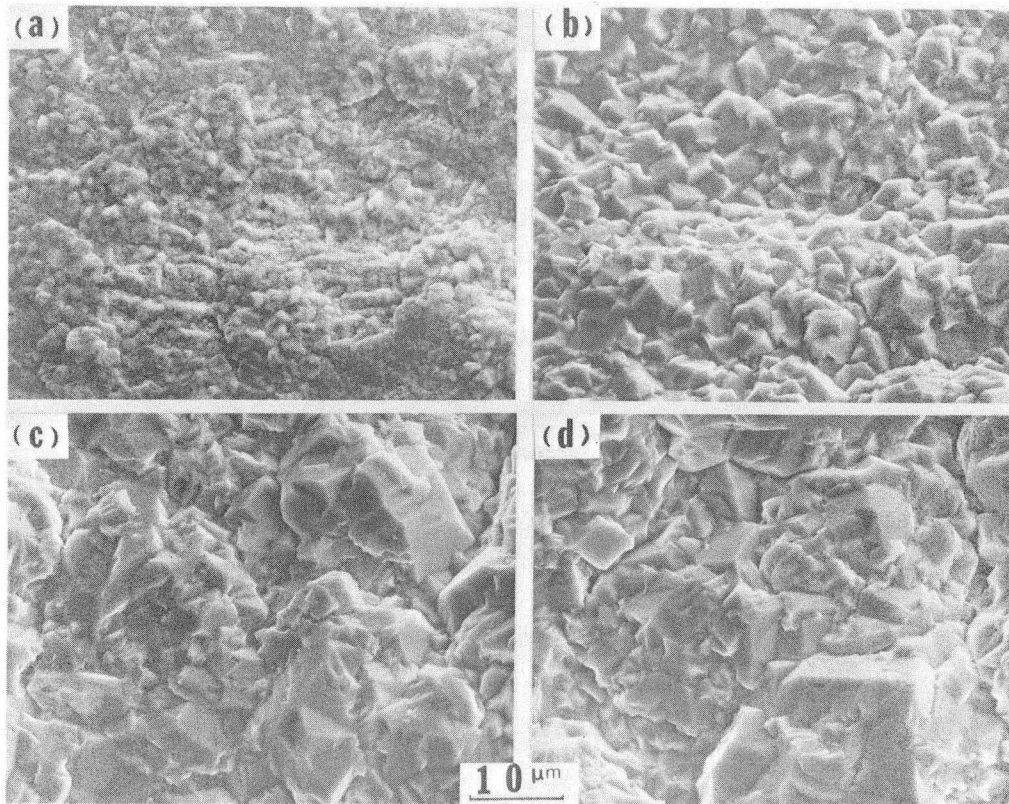
Fig. 2. Scanning electron micrograph of the mechanically polished and chemically etched cross section of GaAs deposited on molybdenum at 800°C with $y_{\text{TMG}} = 0.0017$, and $\text{As/Ga} = 24$.



XBB 769-8370

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 $y_{H_2S} = 1.6 \times 10^{-5}$.

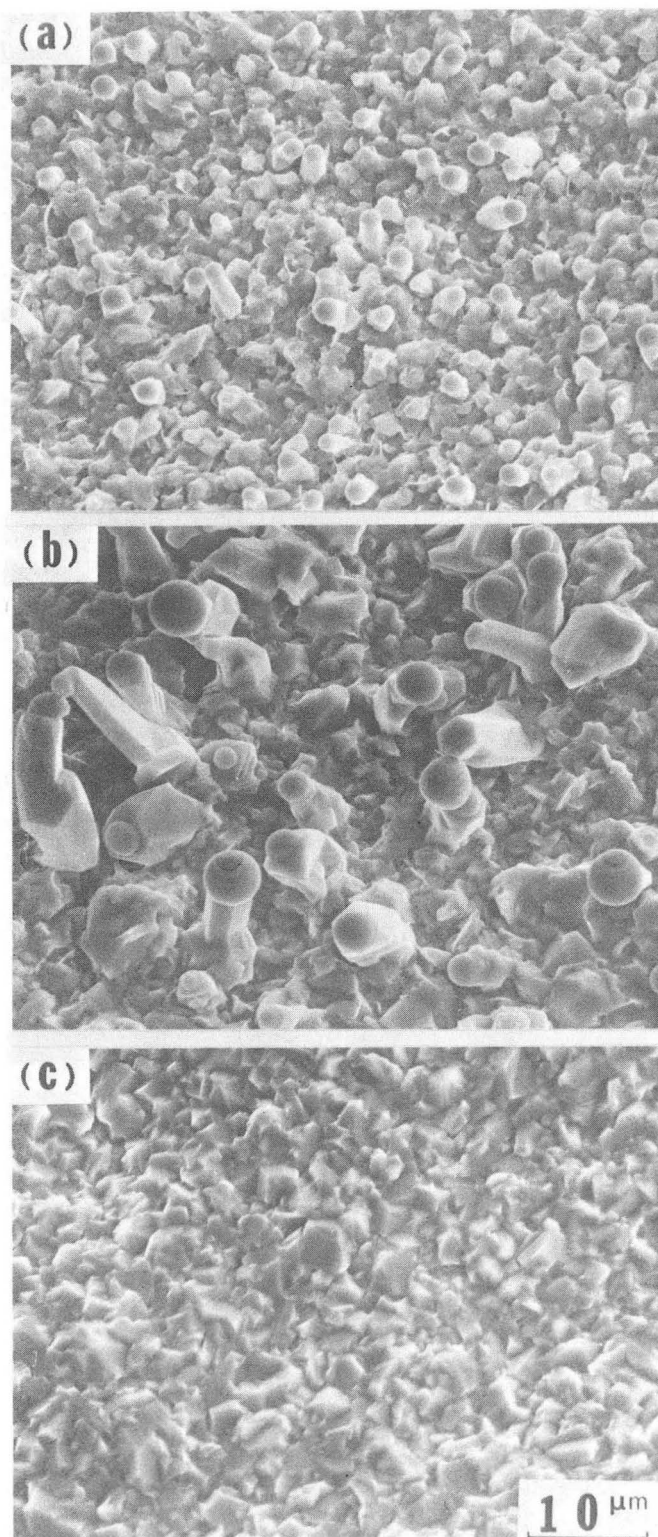
(a) 600°C, (b) 700°C, (c) 875°C, (d) 950°C.



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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.



XBB-769-8374

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

V. PREPARATION OF SCHOTTKY-BARRIER SOLAR CELLS FROM POLYCRYSTALLINE GaAs ON MOLYBDENUM

Polycrystalline GaAs Schottky-barrier solar cells have been prepared by chemical vapor deposition of a 4 μm thick layer of n-type GaAs from an organometallic source onto metallurgical-grade molybdenum, and by sputter deposition of gold. The open-circuit voltage of the device is 0.34 V. The short-circuit current density of 3.7 mA/cm^2 is low because of a high series resistance. The equivalent AM1 efficiency is 1.3% with an anti-reflection coating.

Solar cells generating electricity directly from sunlight are a promising future energy source for terrestrial application. Of the semiconducting materials suitable for solar cells, GaAs is currently one of the most promising¹ because its 1.4 eV band gap lies close to the value yielding maximum photovoltaic conversion efficiency for the solar spectrum, and because the majority of the incident sunlight is absorbed in a thin (2-4 μm) layer. Also, GaAs solar cells have been shown to operate at elevated temperatures without an important reduction of efficiency.²

Single crystal cells have already been prepared using this compound¹⁻³ and efficiency up to 21% have been achieved.² Nevertheless, such single crystal cells remain economically unattractive for terrestrial application,² mainly because of the current high price

of Ga. A way to reduce the cost significantly is to use a thin, polycrystalline film of GaAs deposited on a low-cost substrate, such as graphite or metal.

Some recent work^{4,5} has shown that for columnar grains of a few microns in diameter, the grain boundaries would only moderately affect the performances of the resulting cell. The present work is an extension of previous work by the authors⁶⁻⁸ directed at obtaining thin GaAs films with the required properties for photovoltaic device application. A number of Schottky barrier cells have been prepared from thin films grown by the technique referenced above, and their properties are reported here.

GaAs was deposited by chemical vapor deposition from trimethyl gallium and arsine in a hydrogen carrier gas onto molybdenum sheet. Metallurgical grade (99.9%) molybdenum sheet 1.5 mm thick was used as the substrate. Prior to GaAs deposition, the metal was chemically polished in a 6:2:1 mixture of nitric:lactic:hydrofluoric acid. The substrate was then degreased and placed on a graphite susceptor in a vertical, rf heated reactor. GaAs was deposited at 0.4 $\mu\text{m}/\text{min}$ at 750°C. Samples grown were intentionally doped with S obtained by introducing a flow of H_2S during the growth period. Resulting films were n-type with carrier concentration of about 10^{17} cm^{-3} .

Prior to the barrier formation, the sample was rinsed in hot trichloroethylene and acetone, then etched in a 1% bromine methanol solution, then rinsed, dried and quickly placed in a dc sputtering chamber. A 99.99% gold barrier about 100 Å thick was formed by

sputtering through a metallic mask at room temperature. A gold grid about 1000 Å thick was then sputtered through another metal mask. The grid consisted of fingers 0.5 mm wide and separated from each other by 2.8 mm. The grid fingers were connected together by a perpendicular line 1.3 mm wide. Aluminum wires were bonded to the gold contacts and to the molybdenum substrate with silver paint.

A schematic diagram of the cell is shown in Fig. 1. Scanning electron microscopy of chemically vapor deposited films on molybdenum showed that the polycrystalline layer differed from the ideal structure shown in Fig. 1a, and contained surface defects, as depicted in Fig. 1b. A scanning electron micrograph of an as-deposited 3.7 μm thick GaAs film is shown in Fig. 2.

The spectral response of a completed cell is shown in Fig. 3. The magnitude of the photocurrent response has been arbitrarily normalized to unity. The response is very similar to that obtained with p-n junctions, and the value of the band-gap deduced from this curve is equal to the literature value of 1.4 eV.

The forward-biased, dark voltage-current characteristics obtained at room temperature are shown in Fig. 4. The dark current for a Schottky-barrier diode can be written in the form,⁴

$$J = J_0 \left[\exp \left(\frac{qV}{nkT} \right) - 1 \right] \quad (1)$$

where the saturation current density J_0 is related to the barrier height by

$$J_o = A^{**} T^2 \exp\left(-\frac{q\phi_b}{kT}\right) \quad (2)$$

where A^{**} is the modified Richardson constant. The value of n deduced from Fig. 4 is 14.3. GaAs solar cells usually exhibit values of n near 1, but higher values have already been reported^{9,10} and could be a consequence of tunneling currents⁴ due to a high doping level or, more likely, of a low shunt resistance.

The barrier height, ϕ_b , deduced from the V-I characteristics was found to be 0.51 eV, with the modified Richardson constant A^{**} taken¹² to be $4.4 \text{ A}/(\text{cm}^2 \cdot \text{K}^2)$. The discrepancy in this value of the barrier height from the literature value,⁴ [0.90 V], can be due to small regions with low barrier height on the contact surface,¹³ or to errors inherent in evaluating ϕ_b from the V-I characteristics.

The current-voltage response of the cell under a $100 \text{ mW}/\text{cm}^2$ of water filter tungsten illumination is shown in Fig. 5. The low open circuit voltage, $V_{oc} = 0.34 \text{ V}$, is probably due to a shunt resistance evaluated from Fig. 4 to be $100 \text{ } \Omega/\text{cm}^2$. As mentioned in previous works by the authors^{7,8} their films of CVD deposited GaAs preserve the mechanical defects of the substrate. Therefore, in 3-4 μm thick films, there may remain some zones not completely covered by GaAs; the resulting pores can create the shunt resistance when gold surface contacts are applied.

The low value of the short circuit current, $3.7 \text{ mA}/\text{cm}^2$, and the general shape of the I-V curve suggest a high series resistance of about $70 \text{ } \Omega/\text{cm}^2$, most probably due to a high contact resistance of the

Mo/GaAs interface. An n^+ -GaAs layer between the Mo and the n-GaAs film could reduce the contact resistance.

The maximum output power obtained from the present cells is 0.67 mW/cm^2 which corresponds to an AM1 efficiency of 0.67% and a fill factor of 35%. The cell efficiency corrected for a surface reflection loss of 50% by an anti-reflection coating is 1.3%.

A factor which contributes to the low value of the conversion efficiency in the present cells is the wide spacing of the fingers in the grid pattern. Although the surface film of gold which constitutes the barrier was kept voluntarily thin (100 Å) to minimize the amount of light reflected, the rough surface topography of the GaAs film created gold accumulations of much more than 100 Å as well as gold-free zones. Thus, the only part of the cell which contributes to current generated is located in the immediate vicinity of the grid. The cell efficiency could therefore be increased greatly by establishing CVD conditions favoring lateral growth of GaAs crystallites, and a smooth upper surface.

Polycrystalline, GaAs, Schottky-barrier solar cells fabricated by the chemical vapor deposition of GaAs from an organometallic source onto Mo sheet have been successfully produced with an efficiency of 1.3%. The photovoltaic conversion efficiency with 4 μm thick GaAs films remains low due mainly to a high GaAs/Mo interfacial resistance of about $70 \Omega/\text{cm}^2$, and by shunt resistance of about $100 \Omega/\text{cm}^2$ created by gold shorts through pores in the GaAs film. The conversion efficiency could be increased significantly by the elimination of these problems.

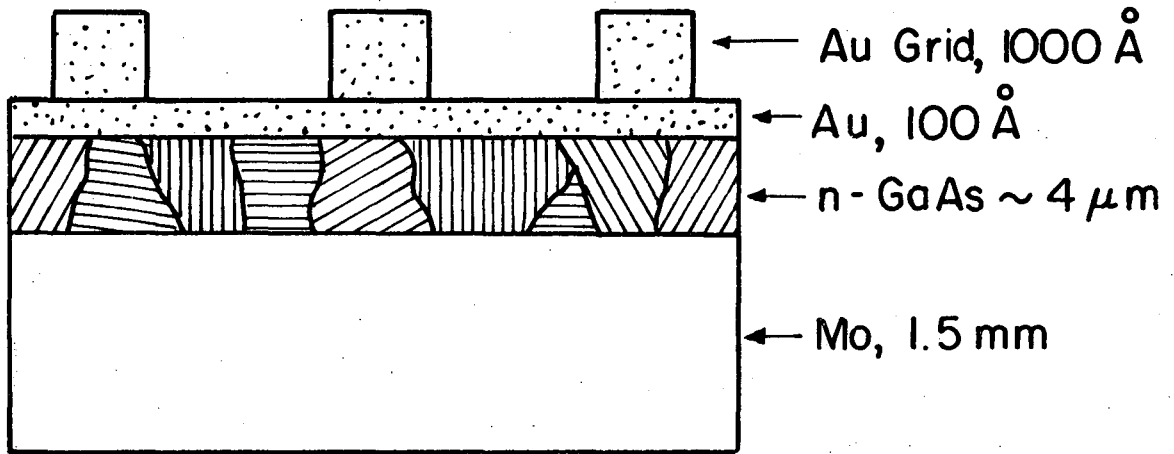
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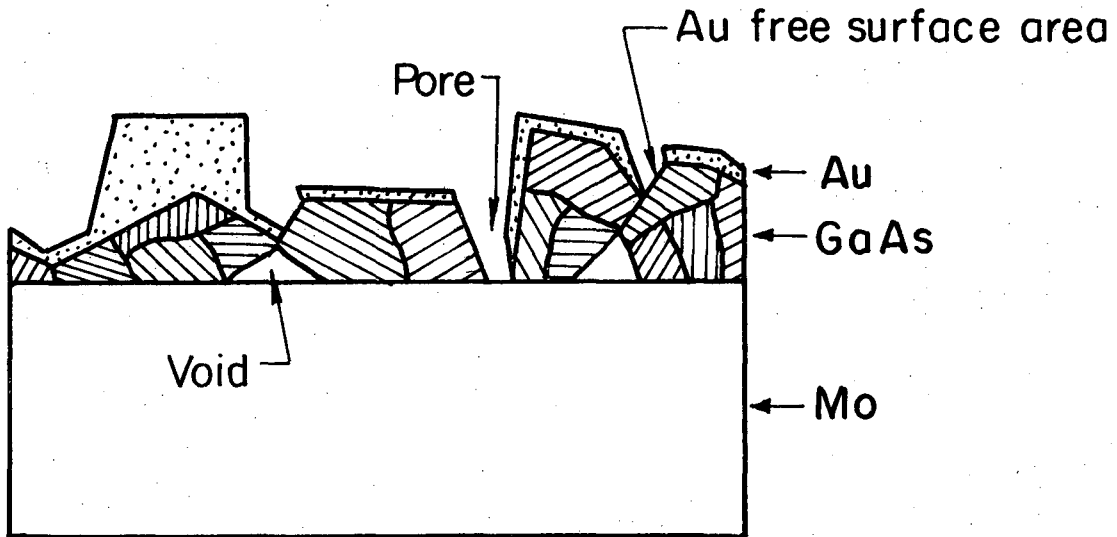
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FIGURE CAPTIONS

- Fig. 1. Schematic cross-section of Schottky-barrier solar cells:
(a) ideal polycrystalline structure;
(b) actual structure showing structural defects.
- Fig. 2. Scanning electron micrograph of chemically vapor deposited GaAs on molybdenum.
- Fig. 3. Spectral response of the Au/n-GaAs/Mo solar cell.
- Fig. 4. Forward-biased, dark V-I characteristics of the Au/n-GaAs/Mo solar cell.
- Fig. 5. V-I characteristics of the Au/n-GaAs/Mo solar cell under water-filtered 100 mW/cm^2 tungsten illumination.



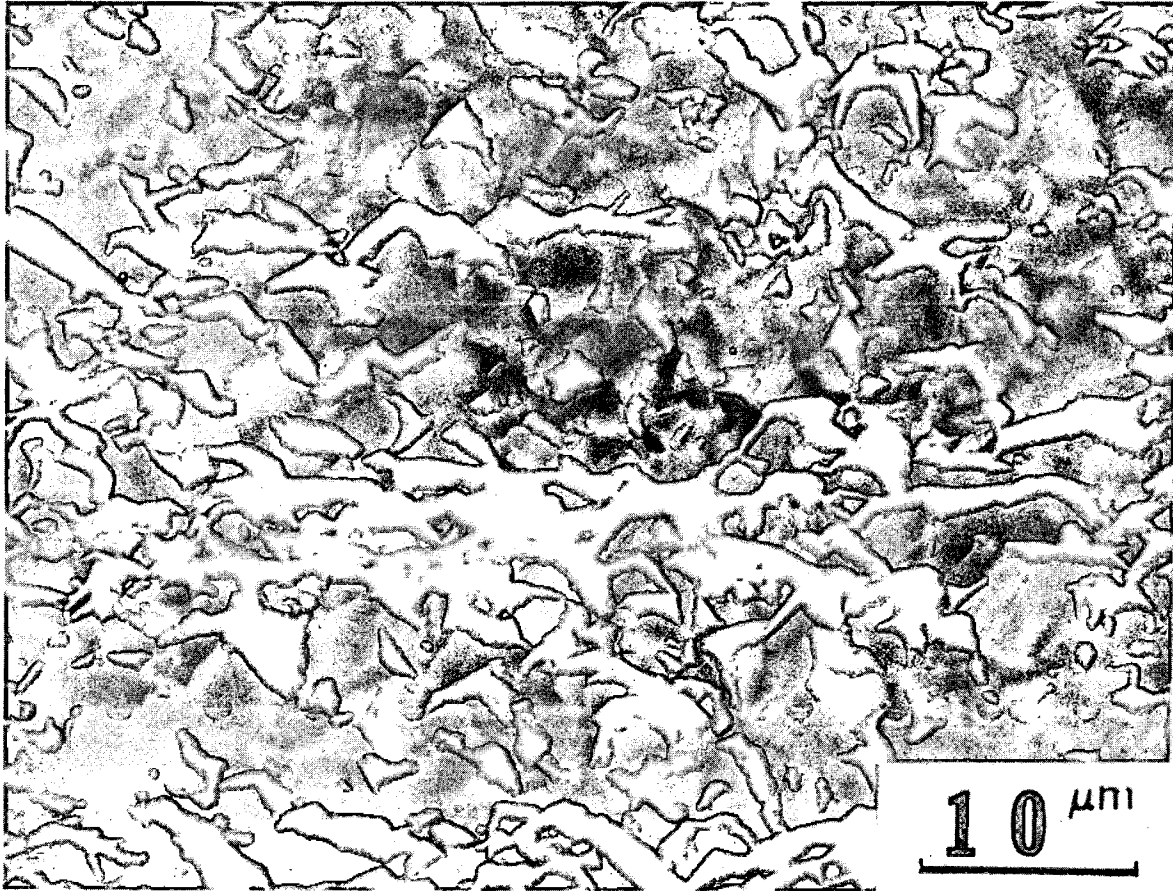
(a)



(b)

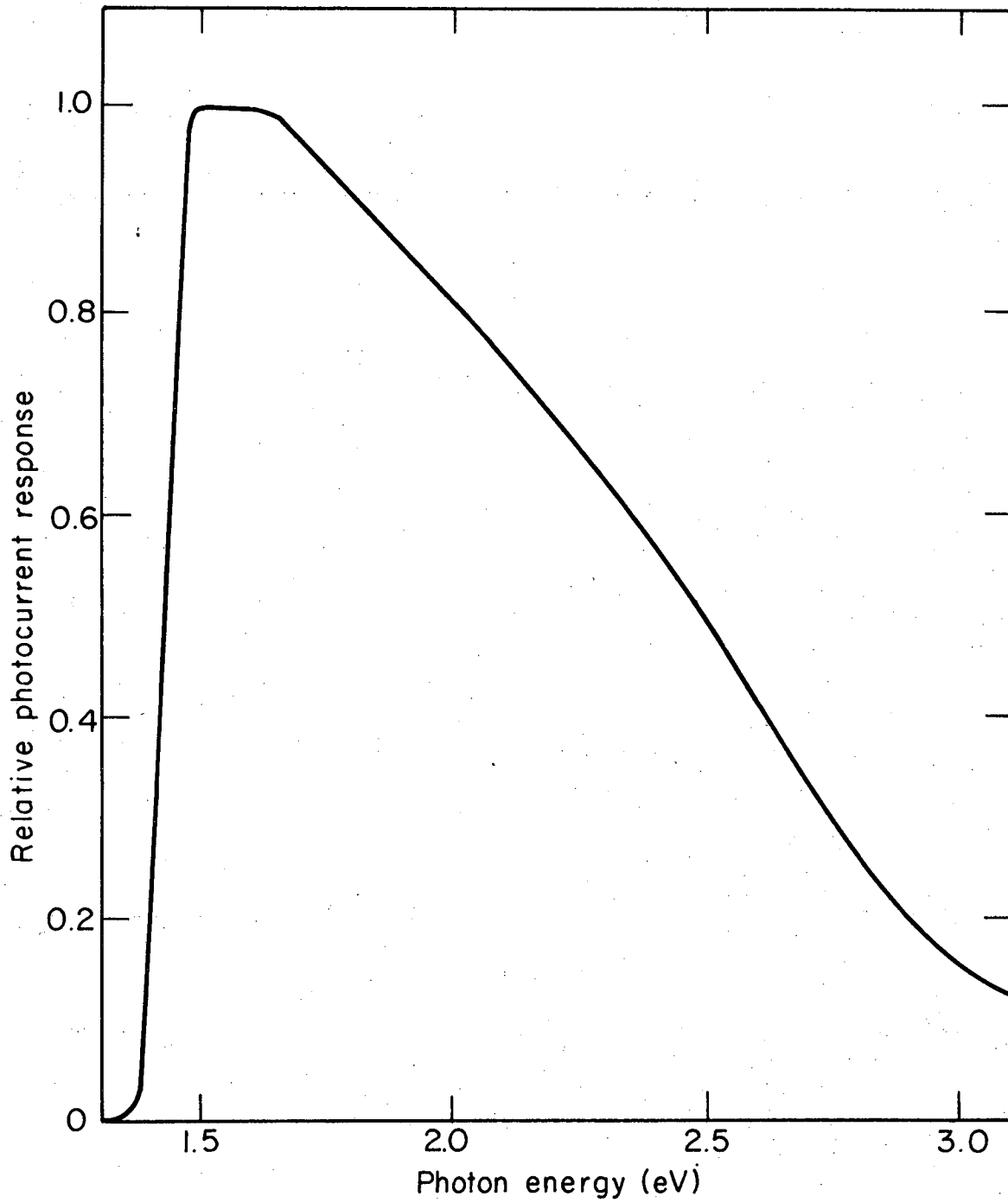
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Fig. 1. Schematic cross-section of Schottky-barrier solar cells:
(a) ideal polycrystalline structure;
(b) actual structure showing structural defects.



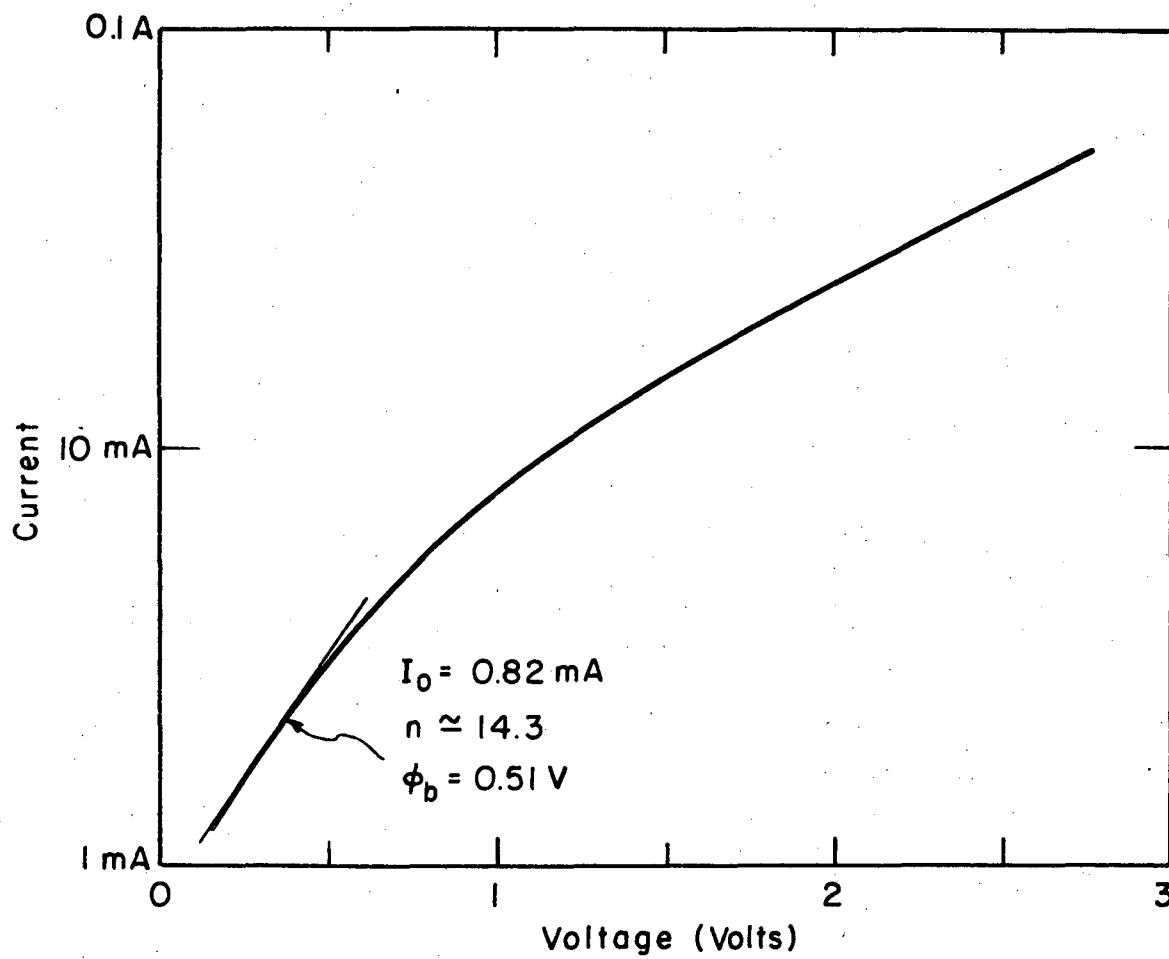
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Fig. 2. Scanning electron micrograph of chemically vapor deposited GaAs on molybdenum.



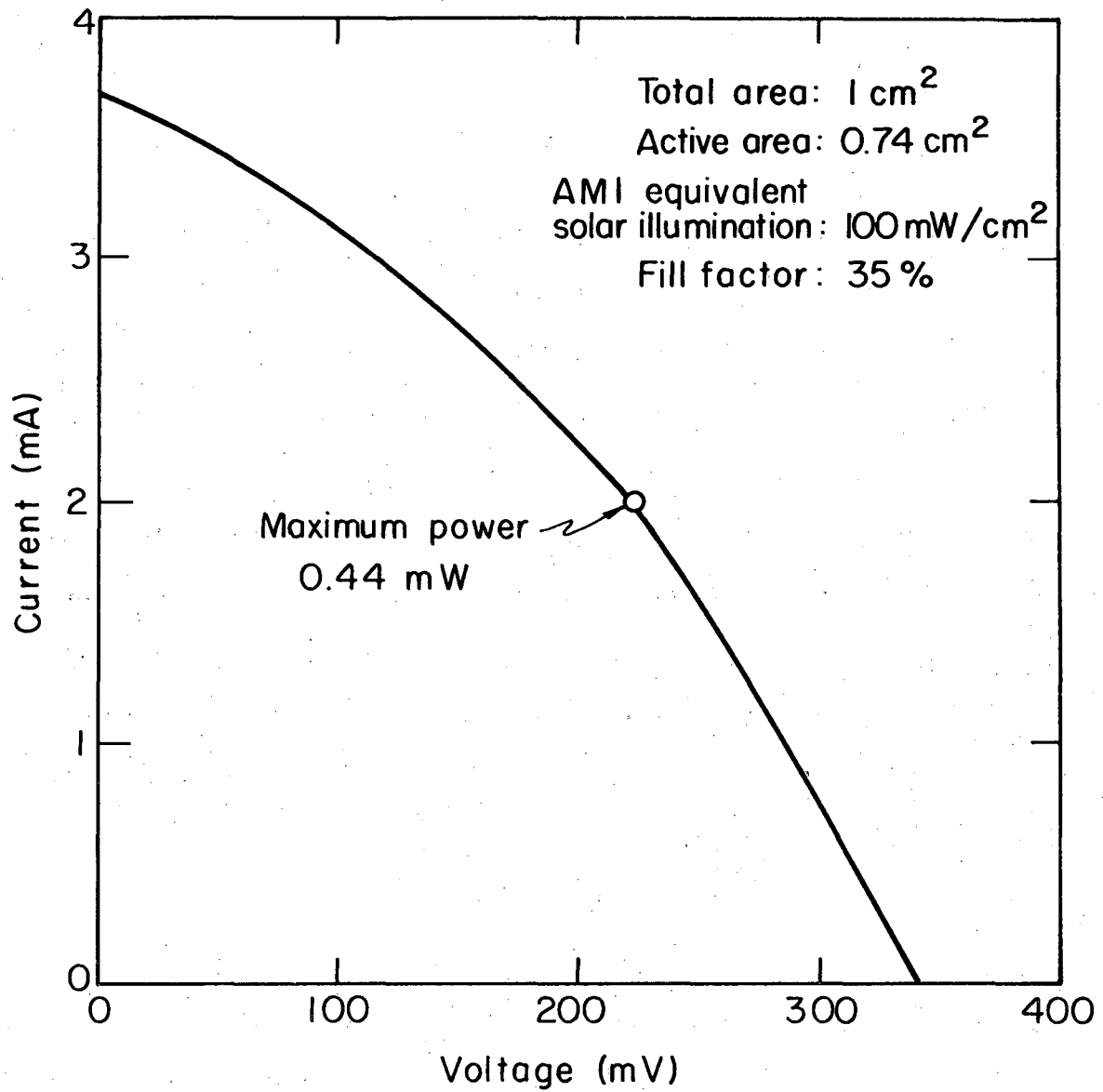
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Fig. 3. Spectral response of the Au/n-GaAs/Mo solar cell.



XBL 7610-7668

Fig. 4. Forward-biased, dark V-I characteristics of the Au/n-GaAs/Mo solar cell.



XBL 7610-7671

Fig. 5. V-I characteristics of the Au/n-GaAs/Mo solar cell under water-filtered 100 mW/cm^2 tungsten illumination.

IV. CONCLUSIONS

In an attempt to prepare thin film solar cells for terrestrial application, GaAs has been deposited experimentally on different substrates by chemical vapor deposition using organometallic trimethyl gallium. A review of the properties of the deposited films with respect to the nature of the substrate has shown that graphite and molybdenum are suitable materials for this application. The study of the influence of growth conditions (substrate temperature, concentration of reactants, concentration of doping gas) on the microstructural properties of deposited layers of GaAs on graphite and Mo has yielded a determination of the optimum conditions of deposition for preparation of solar cells with each substrate material.

Solar cells prepared with graphite always exhibited very low short circuit current, because of a high series resistance. Better results were obtained with Schottky barrier solar cells consisting of a Au/n-GaAs layer deposited on Mo. Efficiencies of 1.3% under equivalent AM1 solar illumination have been achieved for a 1 cm^2 area cell. This efficiency remains low because of a low shunt resistance and a high series resistance in fabricated cells. However, the efficiency could be increased significantly by raising the shunt resistance and, presumably more, by decreasing the series resistance.

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