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# Growth of Polycrystalline GaAs for Solar Cell Applications

**Abstract:** Films of polycrystalline GaAs have been grown on foreign substrates by the metal-organic process. The main objective was to produce films with as large a grain size as possible, so that high-efficiency photovoltaic devices may eventually be fabricated from such thin film/substrate structures. At 973 K the average grain size was less than 1 $\mu$m, and was unaffected by the choice of substrate. Increasing the deposition temperature to 1123 K, while maintaining all other conditions the same, resulted in grains as large as 10 to 20 $\mu$m in diameter. Grain sizes as large as 10 $\mu$m could be obtained by precoating the substrates with thin films of evaporated gold or tin. However, both of these methods gave films that were discontinuous. A two-step procedure in which the films were nucleated at 873 K prior to growth at 1123 K yielded continuous films with an average grain size of 5 $\mu$m. Schottky barrier solar cells fabricated from these films exhibited short-circuit current densities as high as 15.7 mA/cm$^2$, even though the highest conversion efficiency (AM0, uncoated) was only 1.3 percent because of the low fill factor (0.28).

## Introduction

Woodall and Hovel [1] have pointed out that although GaAs yields the best existing and potential solar cells from the standpoint of efficiency, these photovoltaic devices can make an impact on large-scale terrestrial electrical energy generation only if their cost can be drastically reduced. Currently, several academic and industrial institutions are working to bring about such cost reductions; this objective is to be accomplished through a 50- to 100-fold reduction in the amount of GaAs needed for a device and by elimination of the expensive processing used in making single-crystal wafers. The low cost solar cell under study is to have a layer of n-type polycrystalline GaAs 2-5 $\mu$m thick. This layer will be grown on an inexpensive and readily available conductive substrate, to which this layer must make ohmic contact. The polycrystalline GaAs thin film must be continuous and have a columnar grain structure; i.e., essentially all grain boundaries must be normal to the film plane. In addition, average grain size must be at least several $\mu$m in diameter. Lanza and Hovel [2] have calculated that GaAs films 2 $\mu$m thick, consisting of columnar grains with an average diameter of 10 $\mu$m, can be fashioned into Schottky barrier solar cells exhibiting a maximum efficiency of 13.5 percent. Actual efficiencies of three to five percent were reported in 1967 by Vohl et al. [3] for polycrystalline GaAs cells, and this result has not been substantially improved upon since then.

The method chosen for growth of polycrystalline GaAs films was the "metal-organic" vapor deposition process introduced by Manasevit and Simpson [4] and shown by Bass [5] to yield device-quality material. In this process, trimethylgallium vapor and arsine gas are reacted to form GaAs on an rf-heated substrate. The metal-organic process has several advantages, including better process control and less energy consumption, which make it more amenable than other vapor deposition techniques to eventual low cost, large-scale manufacturing. For this reason, this process was chosen over the close-spaced transport scheme used by Vohl et al. [3]. Even though the close-spaced process has produced columnar-grained films and fairly efficient solar cells, it clearly does not have the potential for mass production, whereas the metal-organic process does.

Preliminary experiments showed that films obtained with the metal-organic process were not satisfactory, principally because the grain size was too small. Although high device efficiency is the ultimate objective, the first phase of this study required extensive investigation of film growth; these results are described in this paper.

## Experimental conditions

Most of the films were deposited at 973 K at a rate of 0.5 $\mu$m/min, with gas flows of 1 cc/min $(CH_3)_3Ga$ and

5 cc/min $AsH_3$ in 2500 cc/min $H_2$. These conditions were initially chosen because they are optimal for homoepitaxial growth of GaAs. Later it was discovered that better films were obtained when the growth was first nucleated at 873 K and then completed at 1123 K.

The trimethylgallium $(CH_3)_3Ga$ was maintained in a thermostated bath at 273 K. The vapor deposition system was a 5-cm (inside diameter) vertical reactor such as that shown in Fig. 1. (The provision shown for cooling of the reactor wall was, however, frequently not used.) The susceptor for the rf heating was a cylindrical 2.5-cm slug of SiC-coated graphite. Several different foreign substrates were used, both metals and nonmetals. The purity of the metal substrates was always at least 99.9 percent. Although low substrate cost will ultimately become important, such considerations were ignored at this stage.

Under these conditions, although polycrystalline GaAs films grow very readily on foreign substrates, they do not grow in the desired form, i.e., with large columnar grains. The major task was, therefore, learning to control this grain morphology. This task was approached from three different standpoints: choice of an advantageous substrate, modification of substrate or film, and variation of growth conditions with respect to the "standard" conditions mentioned previously.

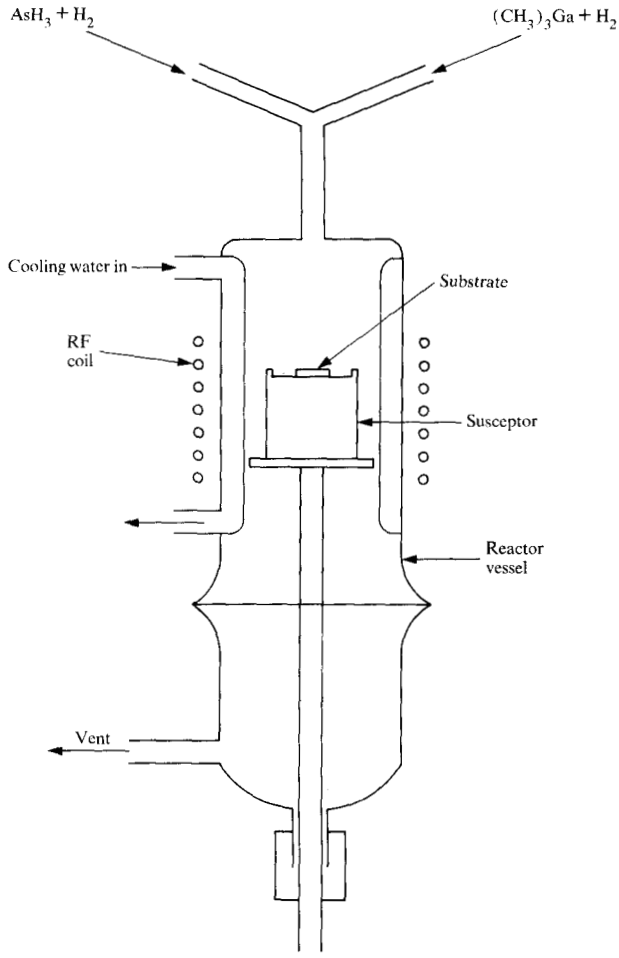



**Figure 1** Schematic of metal-organic vapor growth system.

## Film growth results

• *Choice of substrates*

The first approach was to search for substrates that would favor the growth of large grains by heteroepitaxy. This approach was suggested by a report of expitaxial growth of GaAs on W by Amick [6]. Our growth conditions were as given above. Many substrates were tried, ranging in degree of crystallinity from single-crystalline to amorphous. These included single crystals of Si and W; polycrystalline sheets of W, Mo, and Ta; and vitreous silica and vitreous carbon. The result in every case was essentially the same; neither epitaxy nor oriented growth was achieved. In fact, the single-crystal substrates showed no more orienting tendency than did the amorphous ones. The x-ray pole figures showed no evidence of preferred orientation, and the results with the single-crystal and polycrystalline W substrates were identical.

Figures 2 (a–c) illustrate the morphology of three typical films grown on the polycrystalline substrates W, Ta, and Mo. All three consist of highly faceted grains averaging less than 1 $\mu$m in diameter, with no evidence of texturing. Any observable differences among the three examples can be attributed to run-to-run variations.

The growth mode is depicted in Fig. 3. The films appear to have a "nodular" growth form and consist of dense deposits of very fine, randomly oriented grains having the same morphology on all of the substrates (and even on the susceptor). After nucleation, the microcrystalline nodules expand, coalesce, and finally form a rough-surfaced but otherwise uniform film. Thus, instead of being columnar in nature, most of the GaAs grains have been nucleated and grown on top of one another.

• *Special treatments*

This section deals with the effects produced by certain treatments of either the substrates or of the films themselves. Figures 4 (a–c) illustrate some examples. Figures 4(a) and 4(b) show polycrystalline films grown on Si and Ta substrates that were precoated with evaporated Au (800 nm) and Sn (50 nm), respectively. It can be seen by comparison with Figs. 2(a–c) that much larger grains (up to 10 $\mu$m in diameter) were produced. However, the size distribution is very nonuniform in the Au/Si case; the film is discontinuous in the Sn/Ta case.

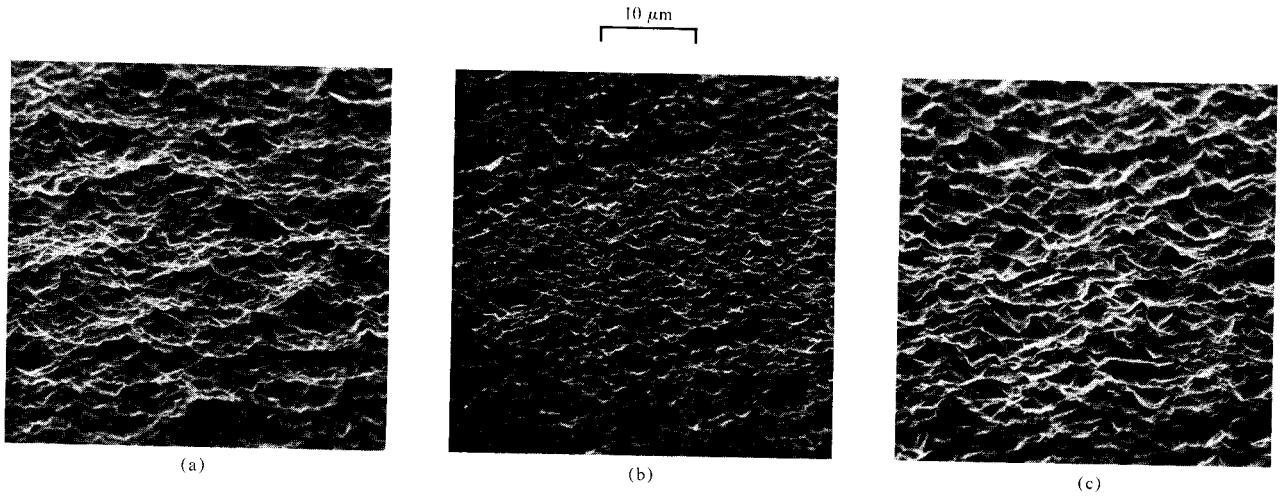



**Figure 2** Scanning electron micrographs of polycrystalline GaAs deposits on three different metals: (a) W, (b) Ta, and (c) Mo.

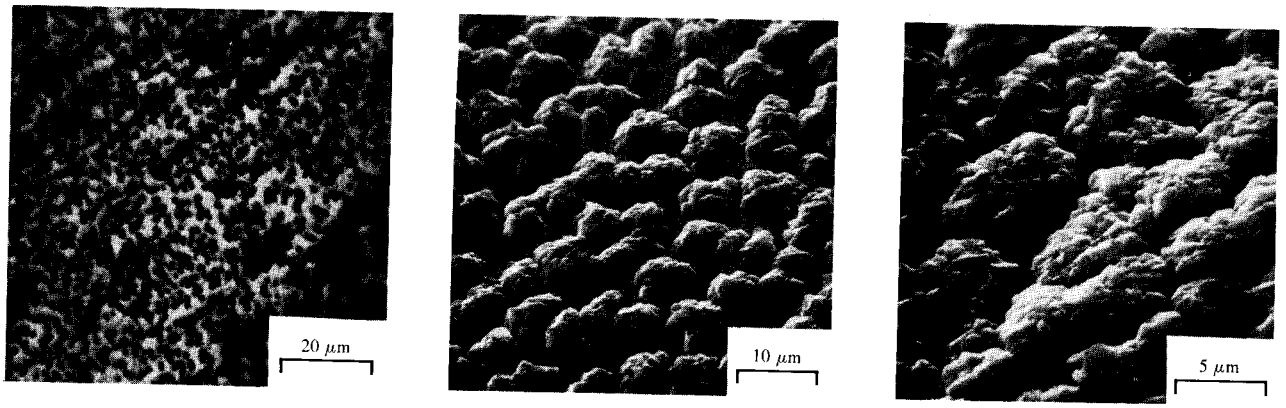
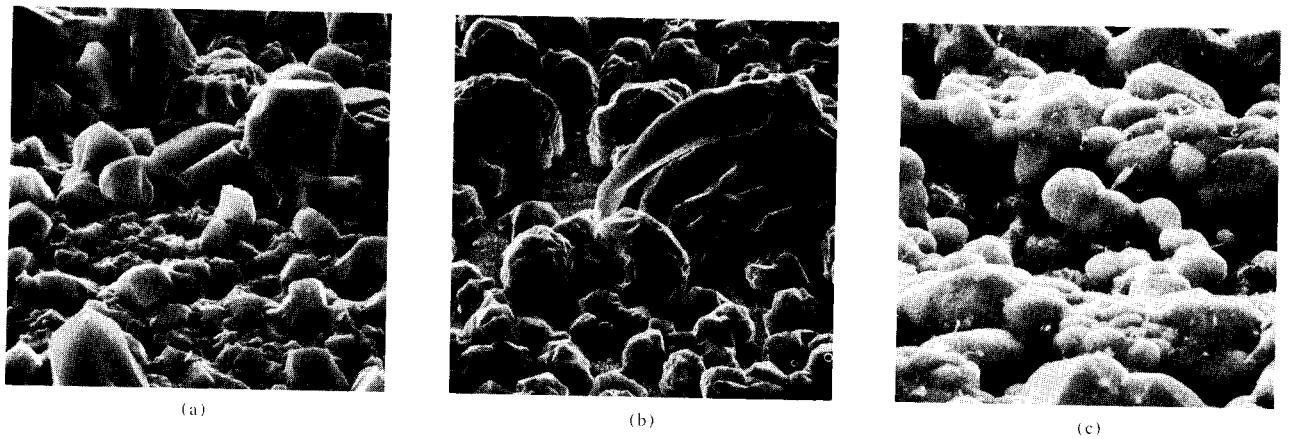



**Figure 3** Nucleation and growth of nodular clusters of polycrystalline GaAs.

**Figure 4** Scanning electron micrographs of GaAs deposits on variously treated substrates. (a) Au on Si, (b) Sn on Ta, and (c) post-heat-treatment, graphite substrate.



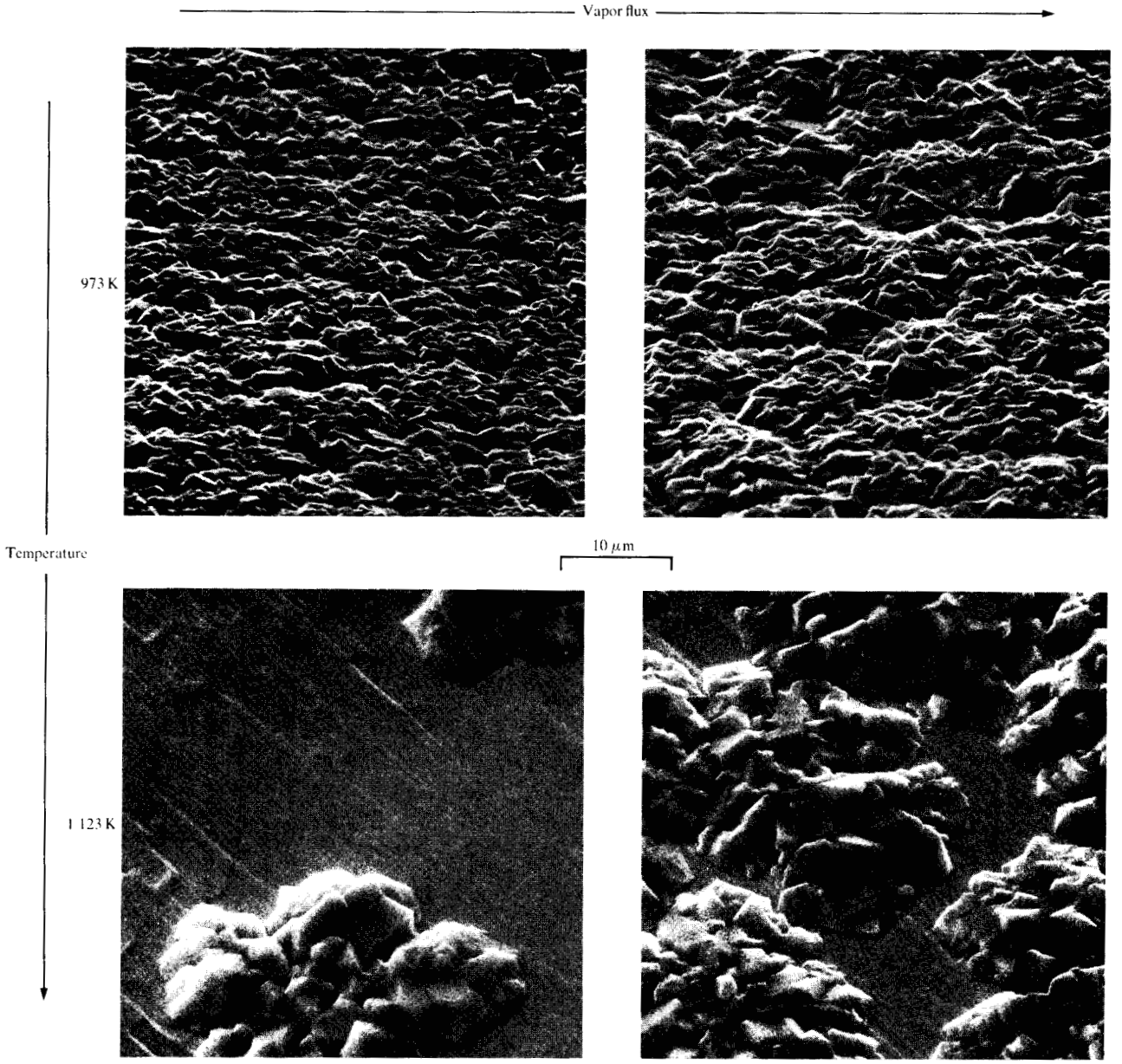



**Figure 5** Effect of varying the reactant flux (supersaturation) and growth temperature on the polycrystalline GaAs grain morphology.

Figure 4(c) shows grain growth in a film of GaAs on graphite. Before heat treatment, this film looked much like the films in Fig. 2. The heat treatment consisted of annealing the specimen for four hours at 1323 K in a sealed tube containing As vapor. Large, rounded grains were produced, but at the expense of film continuity.

Another treatment was to mix HCl gas with the primary reactants. In the $AsCl_3$-Ga-$H_2$ system [7], it is frequently possible to arrange conditions such that deposition occurs only on the single-crystal GaAs substrate. Nucleation on the fused quartz substrate holder is thereby totally inhibited, presumably due to the presence of the Cl atom. It was hoped that the addition of HCl gas to the reactant mixtures would limit the extent of nucleation and thus promote larger grain structures, in addition to providing a cleaner growth environment. However, the addition of

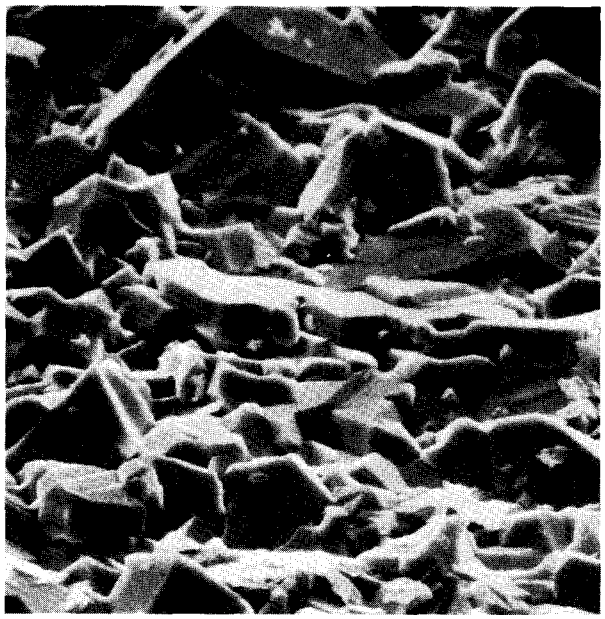



**Figure 6** Scanning electron micrograph of the polycrystalline GaAs film grown by the two-step procedure.

HCl gas [even in a volume equal to that of the $(CH_3)_3Ga$] produced no effect on the nature of the polycrystalline GaAs deposit.

• *Variation of growth conditions*

All the experiments described in the two preceding sections were carried out under approximately the standard growth conditions given earlier. Experiments in which these conditions were varied are now presented. These experiments were conducted with W substrates, but, in view of the effects reported in the previous section, it is unlikely that the particular choice of substrate affected the results.

When the deposition temperature was raised to 1123 K (without using the water jacket), the grain size was increased to approximately 10 μm. However, these large grains were no longer adjacent to one another [see Fig. 5(c)]. This lack of film continuity was due to a decrease in the effective vapor flux of reactants, which was in turn caused by increased deposition on the uncooled walls. Experimental studies of the effects of variations in this effective flux at different growth temperatures showed that this parameter had no effect at 973 K (see Fig. 5). At 1123 K, however, it is seen that, as the vapor flux increases, the grains develop closer together but smaller in size.

On the basis of these observations, a procedure was devised that used the effect of higher growth temperatures to yield larger grains without sacrificing complete substrate coverage. This consisted of nucleating the film at 873 K for 30 seconds and then raising the temperature to 1123 K and continuing the growth for 15 minutes. The best result was a film approximately 4 μm thick with an average grain size of 5 μm, as shown in Fig. 6. When a comparison is made with the films of Fig. 2, at the same magnification, it is clear that the two-temperature process gives a much larger grain size and that the film is still continuous. Furthermore, the resultant grain morphology is a much closer approximation to the ideal columnar structure than in the 973 K case. Scanning electron microscopy of sections cleaved through the films revealed that the proportion of grain boundary oriented parallel or nearly so to the substrate has been vastly reduced.

The result just described was rather difficult to control because of the dependence of vapor flux on reactor-wall temperature. Considerably more control of the process was achieved when the water-jacketed reactor was used. The temperatures were the same but instead of using wall deposition to inadvertently reduce Ga flux during the high-temperature step, this control was effected by reducing the input flow rate of $(CH_3)_3Ga$ by a factor of three. Films grown by this method are also continuous and large-grained and are similar to that shown in Fig. 6.

## Device results

Solar cells were fabricated on some of the films by evaporating many 10-nm-thick semitransparent gold dots onto the sample surface. The response of the Au Schottky barriers to simulated AM0 illumination (average solar irradiance under outer space conditions) was then measured.

For films grown by the single-step process, some of the Schottky devices showed evidence of rectification at the film-substrate interface, and some were short-circuited. This latter problem was absent in films grown by the two-step process, so that solar cell parameters could be measured. The short-circuit current density ($J_{SC}$) of the best device was an encouraging 15.7 mA/cm$^2$, which corresponds to about 70 percent of that typically measured for a Au-GaAs single-crystal Schottky barrier solar cell [8]. However, the open-circuit voltage $V_{OC}$ was 370 mV, in contrast to the 500–750 mV values obtained for single-crystal GaAs devices [9], which, when coupled with a fill factor of 0.28, gave a conversion efficiency of only 1.3 percent (without antireflective coating).

## Discussion

It has been shown that foreign substrates, when used with the metal-organic process under growth conditions that are excellent for homoepitaxy of GaAs, do not induce any heteroepitaxy or preferred orientation in polycrystalline GaAs films. Instead, a dense deposit of very fine, randomly oriented grains is obtained which has the same

morphology on all the substrates and even on the susceptor. This is not the case for other chemical systems, such as the chloride transport method [6], where large, sometimes columnar, grains and even epitaxial growth have been reported; or the close-spaced transport method [3], which yielded columnar grains.

In most vapor deposition systems, a film grows by formation of stable nuclei which then expand coherently, by both surface diffusion and attachment from the fluid phase, until crystallites coalesce into a continuous film. In our experiments, however, a "nodular" form of growth takes place in which an initial small-crystal nucleus serves as the starting point for the piling-up of many more similar small crystals. This type of growth gives rise to many horizontally oriented grain boundaries instead of the desired columnar orientation. This is obviously an undesirable situation from the standpoint of solar cell efficiency.

The different behavior of the metal-organic system compared with that of the others seems to be the result of the very high supersaturation of the reactant gas mixture. The driving force to relieve the supersaturation by polycrystalline deposition is so great that it overwhelms any tendency toward oriented nucleation that some particular substrate might have on the basis of surface energy considerations. The other chemical systems apparently operate in a less supersaturated condition. It is not possible to make a quantitative comparison of these systems with respect to the extent of their vapor supersaturations; the lack of knowledge of the detailed chemistry and thermodynamics of the metal-organic system prevents specification of the equilibrium pressures of the reactant species and therefore the supersaturation.

The fact that, in the single-step process at 973 K, many GaAs grains nucleated and grew on top of one another is also consistent with the assumption of a high supersaturation at the growing surface. Such an assumption does not, however, sufficiently explain the growth mode encountered, since homoepitaxy of GaAs proceeds easily under these same conditions. Thus, it is not clear why the grains, once started, did not propagate in a columnar fashion. It has been suggested [10] that impurity atoms or molecules may build up rapidly on the crystallite faces, "poisoning" them for further epitaxial growth and inducing further nucleation. Possible contaminants could be certain byproducts of the deposition reaction, such as methane ($CH_4$).

Application of vacuum-evaporated thin films of certain metals, specifically Au and Sn in these experiments, was found to be effective in producing very large GaAs grains. The vapor-liquid-solid (VLS) mechanism of crystal growth [11], well known for the role it plays in the growth of whisker crystals, is thought to be responsible for this. In order for VLS to be active in the catalysis of vapor deposition, a molten phase must be present, serving both as a sink for the vapor nutrient species, and as a saturated source for crystallization. Columnar crystals usually grow out of such a melt. The respective liquid phases in the experiments were Sn (mp 505 K) and Au/GaAs (forms alloys at temperatures as low as 673 K [12]).

It was found that the films produced with the metal precoats, although containing large crystals, were nonuniform (Au/Si) or discontinuous (Sn/Ta). In solar cell structures, these situations would lead to high contact resistance or to device shorting, respectively. For these reasons the approach was dropped. However, the subject was not exhaustively studied, and it is possible that a systematic variation of the metal pre-coat thickness at different growth temperatures could lead to large-grained deposits.

Single-step experiments using several different substrate materials and/or growth conditions were never successful in producing large-grained films that were continuous and pinhole-free. Low temperature growth gave a dense deposit of tiny grains while higher-temperature growth yielded much larger grains but incomplete coverage of the substrate. This suggested a strong dependence of nucleation on the effective vapor flux, or supersaturation. Investigations of this dependence were carried out in the uncooled vessel, where flux variations occurred inadvertently, and in the cold-wall vessel, where the flux was controlled independently of the temperature. The results confirmed that supersaturation is the primary variable responsible for controlling both the grain size and the amount of substrate coverage.

From these considerations, a two-step growth process has been developed. The first step must form small nuclei with spacings of a few $\mu$m. This is accomplished by using a condition that favors easy nucleation, but for only a short time (873 K, 1 cc/min $(CH_3)_3Ga$, 30 s). The second step is to grow these nuclei into large crystals by using a condition that does not favor additional nucleation. This condition is achieved by growing at 1123 K and 1 cc/min $(CH_3)_3Ga$ in the hot-wall vessel or 1/3 cc/min in the cold-wall vessel; the cold-wall process is preferred because it is more controllable. This method reproducibly yields films that are continuous, are approximately columnar, and have an average grain size of 5 $\mu$m.

Solar cell studies with polycrystalline GaAs films have been very limited because of the difficulties in growing such films. The best device had a measured AM0 efficiency (uncoated) of only 1.3 percent. With the availability of uniform large-grained films, device studies can now be accelerated. It is expected that such increased emphasis, coupled with further improvements in crystal growth, will soon lead to better devices. A necessary step in this direction is establishment of control over the film doping. This will help, in particular, to give higher and more uni-

form voltages. The attained short-circuit current of 15.7 mA/cm$^2$ is very encouraging. Finally, the problem of the low fill factor (usually associated with series resistance) can probably be alleviated by doping the film-substrate interface and by reducing the incidence of transverse grain boundaries.

## Conclusions

It has been shown that polycrystalline GaAs films consisting of the desired large and approximately columnar grains can be obtained with the metal-organic process; these are basic criteria for fabricating useful photovoltaic devices. Since it is easy and fairly economical to scale up, it would appear that the metal-organic process readily lends itself to the ultimate manufacture of inexpensive solar cells.

In order to achieve the desired results, it was necessary to modify the film growth procedure considerably from that customarily used for single-crystal growth. The chemistries of the various growth reactions strongly influence the grain morphologies, dictating that different reaction conditions must be used for optimum results with the various growth systems. In the conventional single-step deposition process with the metal-organic system, the mode of growth is such that large grains occur only when the nuclei are widely separated; however, this usually leads to incomplete coverage of the substrate. This problem has been solved by a two-step method wherein the spacing of the nuclei is controlled to give continuous films of large grains. Since the vapor supersaturation values are critical in this process, such parameters as reactor-wall temperature and system geometry must be carefully controlled.

Preliminary studies show that Schottky barrier solar cells made from these films have a good $J_{SC}$, but low values for the $V_{OC}$ and fill factor. Improved control of the doping level should increase the conversion efficiency over its present value of 1.3 percent.


## Acknowledgments

We thank H. J. Hovel for fabricating and testing the Schottky barrier devices, and M. C. Blakeslee for providing the scanning electron micrographs.


## References


1. J. M. Woodall and H. J. Hovel, "Outlooks for GaAs Terrestrial Photovoltaics," *J. Vac. Sci. Technol.* **12**, 1000 (1975).
2. C. Lanza and H. J. Hovel, "Efficiency Calculations for Thin-Film Polycrystalline Semiconductor Schottky Barrier Solar Cells," *IEEE Trans. Electron Devices* **ED-24**, 392 (1977).
3. P. Vohl, D. M. Perkins, S. G. Ellis, R. R. Addiss, W. Hui, and G. Noel, "GaAs Thin Film Solar Cells," *IEEE Trans. Electron Devices* **ED-14**, 26 (1967).
4. H. M. Manasevit and W. I. Simpson, "The Use of Metal-Organics in the Preparation of Semiconductor Materials, I. Epitaxial Gallium-V Compounds," *J. Electrochem. Soc.* **116**, 1725 (1969).
5. S. J. Bass, "Device Quality Epitaxial Gallium Arsenide Grown by the Metal Alkyl-Hydride Technique," *J. Cryst. Growth* **31**, 172 (1975).
6. J. A. Amick, "Growth of Single-Crystal Gallium Arsenide Layers on Germanium and Metallic Substrates," *RCA Rev.* **24**, 555 (1963).
7. D. W. Shaw, "Gas Phase Composition and Extraneous Deposition in GaAs Vapor Epitaxy," *J. Cryst. Growth* **35**, 1 (1976).
8. H. J. Hovel, "Diffusion Length Measurement by a Simple Photoresponse Technique," *Conference Record, 12th IEEE Photovoltaic Specialists Conference* (Baton Rouge, LA), 1974, p. 913.
9. R. J. Stirn and Y. C. M. Yeh, "Technology of GaAs Metal-Oxide-Semiconductor Solar Cells," *IEEE Trans. Electron Devices* **ED-24**, 476 (1977).
10. A. A. Chernov, Institute of Crystallography, Moscow, private communication.
11. R. S. Wagner and W. C. Ellis, "Vapor-Liquid-Solid Mechanism of Single Crystal Growth," *Appl. Phys. Lett.* **4**, 89 (1964).
12. J. Guylai, J. W. Mayer, V. Rodriguez, A. Y. C. Yu, and H. J. Gopen, "Alloying Behavior of Au and Au-Ge on GaAs," *J. Appl. Phys.* **42**, 3578 (1971).



*Received October 17, 1978; revised March 3, 1978*



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