SAN-1284-T2

GALLIUM ARSENIDE THIN FILMS ON TUNGSTEN/GRAPHITE SUBSTRATES PHASE II

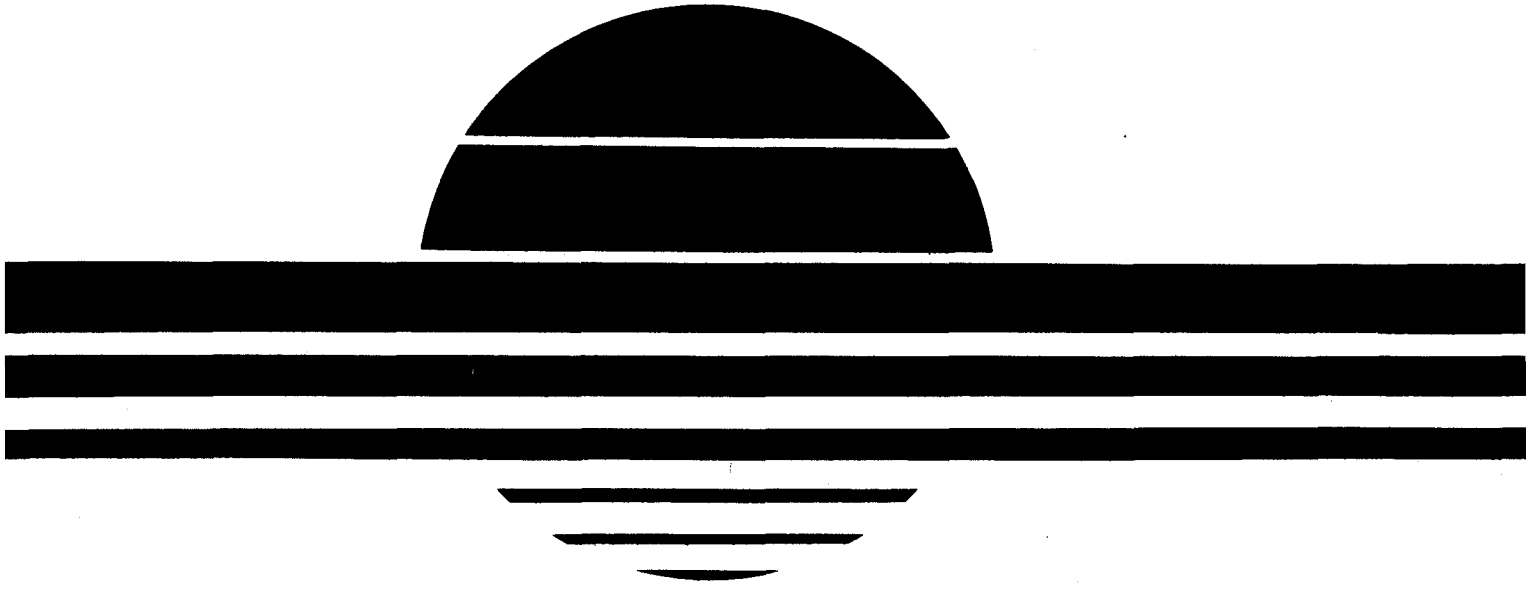
Final Report, September 1, 1977—November 30, 1978

By
Shirley S. Chu

November 1978

Work Performed Under Contract No. EY-76-C-03-1284

Southern Methodist University
Dallas, Texas



U.S. Department of Energy

Solar Energy

NOTICE

SAN-1284-T2
Distribution Category UC-63e

GALLIUM ARSENIDE THIN FILMS ON TUNGSTEN/GRAPHITE SUBSTRATES: PHASE II

Final Report

For Period September 1, 1977 to November 30, 1978

Prepared under DOE Contract EY-76-C-03-1284

by

Shirley S. Chu, Principal Investigator
Southern Methodist University
Dallas, Texas 75275

November, 1978

CONTENTS

List of Illustrations

Summary

This is the Final Report of a research program "Gallium Arsenide Thin Films on Tungsten/Graphite Substrates," covering the period September 1, 1977 - November 30, 1978, supported by the U. S. Department of Energy under Contract No. EY-76-C-03-1284. The objectives of this contract are to investigate thin films of gallium arsenide on low cost substrates and to prepare solar cells with an AM1 efficiency of 6% or higher by August 1978.

Efforts during this year have been directed to (1) the deposition and characterization of gallium arsenide films on tungsten/graphite and graphite substrates, including the initial stage of the deposition process, (2) the effects of the addition of hydrogen chloride to the reactant mixture on the microstructure of gallium arsenide, (3) the deposition of titanium dioxide films as antireflection coatings, (4) the fabrication and characterization of gallium arsenide solar cells on tungsten/graphite and graphite substrates, and (5) the investigation of the temperature coefficients and stabilities of thin film gallium arsenide MOS solar cells.

The use of the reaction between gallium, hydrogen chloride, and arsine in a hydrogen flow has been continued for the deposition of gallium arsenide. The initial stage of the deposition of gallium arsenide on tungsten/graphite substrates consists of a high density of small crystallites while that on graphite is characterized by isolated, relatively large crystallites. The crystallite size in gallium arsenide films can be increased by the addition of hydrogen chloride to the reactant mixture.

The electrical properties of gallium arsenide films, doped with various concentrations of sulfur, on graphite substrates have been investigated in detail. Although the n-GaAs/graphite interface is rectifying, the voltage drop across the interface can be reduced sufficiently for solar cell purposes by using a heavily doped layer at the interface.

The deposition of titanium dioxide films as antireflection coatings has been carried out by the hydrolysis of tetraisopropyl titanate. The fabrication and characterization of large area (9 cm^2) thin film MOS solar cells have been carried out extensively using silver or gold as the barrier metal. Solar cells on tungsten/graphite substrates have an AM1 efficiency of about 6.5% and those on graphite substrate have an AM1 efficiency of about 6%. Thus, the objective of this phase of the contract has been fulfilled.

Preliminary studies in the temperature coefficients and stability of thin film gallium arsenide solar cells have been carried out.

I. Introduction

This is the Final Report of a research program "Gallium Arsenide Thin Films on Tungsten/Graphite Substrates," covering the period September 1, 1977 - November 30, 1978, supported by the Division of Solar Technology of the U. S. Department of Energy under Contract No. EY-76-C-03-1284. The objectives of this contract are to perform intensive studies concerning thin films of gallium arsenide on tungsten/graphite substrates and to prepare reproducibly thin film gallium arsenide solar cells with an AM1 efficiency of 6% or higher by August 1978.

The principal approach used in this program is the deposition of gallium arsenide films on low-cost foreign substrates by the reaction of gallium, hydrogen chloride, and arsine in a hydrogen atmosphere in a gas flow system. Tungsten-coated graphite and germanium films recrystallized on tungsten/graphite were used as substrates for the deposition of gallium arsenide films during the first phase of this program. Graphite was initially selected as a substrate because of its relatively low cost, chemical inertness, and high electrical conductivity. However, the gallium arsenide (no intentional doping)/graphite interface was found to be rectifying, and a tungsten interlayer was used to provide an ohmic contact to gallium arsenide (gallium arsenide/tungsten and tungsten/graphite interfaces have low electrical resistance). Recrystallized germanium films appeared to be a more attractive substrate since the lattice parameter and thermal expansion coefficient of germanium (5.657Å, $5.9 \times 10^{-6} °C^{-1}$) are very similar to those of gallium arsenide (5.654Å, $6.8 \times 10^{-6} °C^{-1}$). Tungsten/graphite was also used as a support for the deposition and recrystallization of

germanium films (tungsten interlayer was used to increase the molten germanium/substrate interfacial tension.

During the first phase of this program, major efforts were directed to (1) chemical vapor deposition of gallium arsenide, (2) the preparation of tungsten/graphite and germanium(recrystallized)/tungsten/graphite substrates, (3) the deposition and characterization of gallium arsenide on tungsten/graphite substrates, (4) the fabrication and characterization of thin film gallium arsenide Schottky barrier solar cells on tungsten/graphite substrates, and (5) the deposition and characterization of gallium arsenide films on germanium(recrystallized)/tungsten/graphite substrates and the fabrication of solar cells. The results are briefly reviewed below.[1]

Two systems for the deposition of gallium arsenide by the reaction of gallium, hydrogen chloride, and arsine in a hydrogen atmosphere were constructed. The reaction tube was a horizontal fused silica tube of 55 mm ID and was heated in a four-zone or five-zone furnace. To evaluate the capability of the deposition systems, single crystalline gallium arsenide and germanium slices with main faces of a {100} orientation were used as substrates for the deposition of gallium arsenide. Under optimized conditions, single crystalline epitaxial gallium arsenide films of good structural perfection have been obtained in all cases, indicating the satisfactory performance of the deposition systems.

The deposition of tungsten on graphite was carried out by the thermal reduction of tungsten hexafluoride with hydrogen in the temperature range of 450-750°C. Tightly adherent films of tungsten were obtained in all cases at rates of up to 1 μm/min. The microstructure and crystallographic properties of tungsten films depend strongly on the deposition temperature.

The size of crystallites increases with increasing temperature, up to 20 μm in tungsten films deposited at 700°C. The deposition of germanium was carried out by the thermal reduction of germanium tetrachloride with hydrogen in the temperature range of 750-900°C. Germanium films deposited on graphite consist of small crystallites and cannot be recrystallized as such because of the low graphite/germanium interfacial tension. Germanium films were deposited in situ on tungsten/graphite substrates; the germanium/tungsten interfacial tension is sufficiently large to overcome the surface tension of molten germanium. Large grain germanium films with a strong {111} preferred orientation were obtained by the unidirectional solidification of germanium films on tungsten/graphite substrates.

Gallium arsenide films have been deposited on tungsten/graphite substrates under a wide range of substrate temperature and reactant composition, their structural and electrical properties evaluated, and the deposition conditions optimized. These films are essentially polycrystalline with no appreciable preferred orientations. The crystallite size depends on deposition temperature and film thickness, up to 25 μm in some cases. Films deposited with no intentional doping are n-type with carrier concentrations in the range of 10^{16} to $10^{17}cm^{-3}$ at room temperature, as determined by differential capacitance measurements. Schottky barriers prepared by the evaporation of gold and silver on gallium arsenide films without intentional doping do not show ideal behavior due to their high series resistance, and the series resistance was reduced substantially by using sulfur as a dopant during the initial stage of gallium arsenide deposition to yield a carrier concentration of 10^{18} or higher. MOS type solar cells were prepared from n-GaAs/n^+-GaAs/W/graphite structures by

oxidation with (1) an argon-oxygen mixture and (2) water vapor followed by the formation of gold Schottky barriers and silver grid contacts. Solar cells of 9 cm^2 area have AM1 efficiencies of up to 3.5%. The minority carrier diffusion length in gallium arsenide films deduced from spectral response measurements is in the range of 0.5-0.7 μm.

The formation of low resistance ohmic contacts for polycrystalline gallium arsenide films on tungsten/graphite substrates have been investigated by using a number of evaporated films of metals or alloys in combination with heat treatment. The contact materials investigated were tin, indium, tin-indium, silver-indium-germanium, silver-indium-zinc, gold-germanium, and aluminum-germanium. The resulting contacts on gallium arsenide films with no intentional doping were non-ohmic and those on doped gallium arsenide films were sometimes ohmic, but not reproducible. The application of a capacitor discharge between one pair of contacts often resulted in the penetration of contact material through gallium arsenide films. The difficulty involved in the formation of ohmic contacts is related presumably to the oxide film on the surface of gallium arsenide.

Gallium arsenide films deposited on germanium(recrystallized)/tungsten/graphite substrates are epitaxial with respect to the substrate. However, they contain high concentrations of germanium, about $10^{17} cm^{-3}$. Solar cells from these films have poor characteristics due presumably to the autodoping effect associated with the halide process and the high diffusion rate of germanium along grain boundaries. Because of these problems, the use of germanium(recrystallized)/tungsten/graphite substrates was discontinued.

During the past year, efforts have been directed to (1) the deposition and characterization of gallium arsenide films on tungsten/graphite

substrates by the arsine and arsenic processes, (2) the deposition and characterization of gallium arsenide films on graphite substrates, (3) the effects of the nature of substrates on the initial stage of the deposition process, (4) the effect of the addition of hydrogen chloride to the reactant mixture on the microstructure of gallium arsenide films, (5) the construction and operation of an apparatus for the deposition of titanium dioxide films as antireflection coatings, (6) the fabrication and evaluation of MOS solar cells on tungsten/grahpite and graphite substrates, and (7) the investigation of the temperature coefficients and stabilities of thin film gallium arsenide MOS solar cells. The experimental procedures and results are discussed in the following sections.

II. Chemical Vapor Deposition of Gallium Arsenide on Tungsten/Graphite Substrates

The chemical vapor deposition technique in a gas flow system has been used extensively for the deposition of gallium arsenide films. The most commonly used inorganic reactions for the deposition of gallium arsenide films include: (a) hydrogen chloride, gallium, and arsenide,[2] (b) arsenic trichloride, hydrogen, and gallium,[3] (c) hydrogen chloride, gallium, and arsine,[4] and (d) gallium trichloride, hydrogen, and arsenic.[5] Reaction (c) has been used in most of the deposition experiments because of its simplicity and low cost. However, the impurity content in commercial arsine sometimes varies, thus affecting the carrier concentration in deposited gallium arsenide films. To minimize these variations, reaction (a) has also been investigated since arsenic is readily available in purities of higher than 99.999%.

The majority of the deposition experiments has been carried out using tungsten-coated graphite as the substrate. Grade DFP and TRA graphite (procured from POCO Graphite Incorporated, Decatur, Texas 76234), with similar thermal expansion coefficient as gallium arsenide, was coated with tungsten by the thermal reduction of tungsten hexafluoride, as described in the First Annual Report.[1] Briefly, the deposition was carried out in a fused silica reaction tube of 55 mm ID. The graphite substrates were supported on a graphite susceptor in the reaction tube, and the susceptor was heated externally by an rf generator. They were first heated in hydrogen at 1100-1200°C to remove the surface contaminations. The deposition of tungsten was carried out in the temperature range of 450°-750°C using hydrogen and tungsten hexafluoride at 25 ℓ/min and 30 mℓ/min,

respectively. Tightly adherent films of tungsten were obtained at rates of up to 1 μm/min. The microstructure and crystallographic properties of tungsten films depend strongly on the deposition temperature, and the size of crystallites increases with increasing temperature. Crystallites as large as 20 μm have been observed in tungsten films of 20-30 μm thickness deposited at 700°C. However, most tungsten films were deposited at 500° and were of 2-3 μm thickness, and the average size of crystallites is 1-2 μm. X-ray diffraction examinations indicated that tungsten films deposited at 700°C showed a strong {211} preferred orientation while those deposited at 500°C showed a strong {100} preferred orientation.

II.1 The Gallium-Hydrogen Chloride-Arsine Process

The gallium-hydrogen ehloride-arsine process is widely used for the manufacture of gallium arsenide and gallium arsenide phosphide light-emitting diodes. In this process, a two-zone furnace is used to maintain gallium at 800-850°C and the substrates at 750-800°C. Hydrogen chloride is used to convert gallium into gallium monochloride which reacts with arsine on the substrate surface to deposit gallium arsenide. The chemical reactions are:

$$2Ga(\ell) + 2HCl(g) \rightarrow 2GaCl(g) + H_2(g)$$

$$GaCl(g) + AsH_3(g) \rightarrow GaAs(s) + HCl(g) + H_2(g)$$

II.1.1 Experimental

The apparatus used for the deposition of gallium arsenide films by the gallium-hydrogen chloride-arsine process is shown schematically in Figure 1. It consists of two parts: (a) a gas flow control panel using flowmeters and valves to control the flow of the reactants (hydrogen, hydrogen chloride, and arsine) and dopants (hydrogen sulfide as the

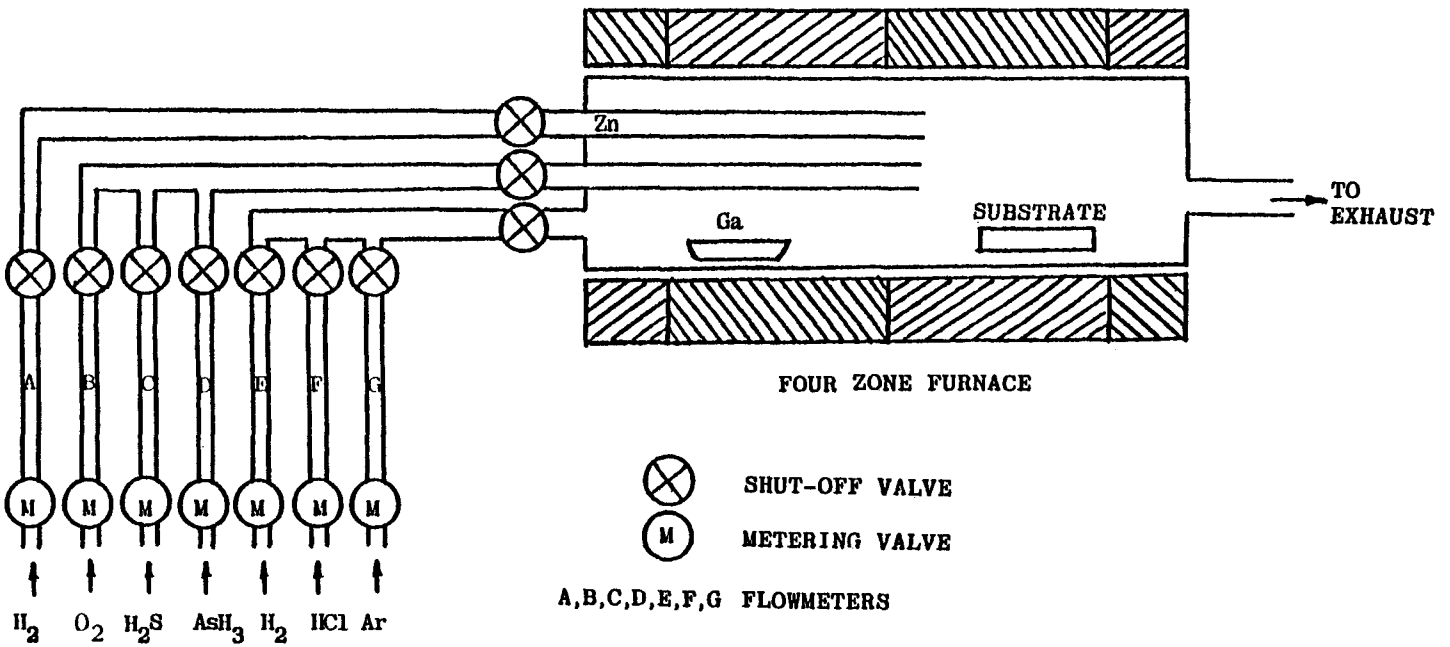


Figure 1 Schematic diagram of the apparatus for the chemical vapor deposition of gallium arsenide films by the halide process.

n-type dopant, and zinc carried by hydrogen as the p-type dopant), and (b) a fused silica reaction tube of 55 mm ID and 59 mm OD held in a four-zone or a five-zone resistance-heated furnace with each zone separately heated and controlled. The temperature profile and the composition and flow rate of the reactant mixture are important factors affecting the deposition rate of gallium arsenide.

To carry out the deposition of gallium arsenide, a gallium container and the substrate are placed in the appropriate temperature zones. A hydrogen-hydrogen chloride mixture is introduced into the reaction tube over the gallium container. At the same time, arsine is introduced into the reaction zone near the substrate surface. The reaction between gallium monochloride and arsine on the substrate surface deposits gallium arsenide. The process parameters include the temperatures of the substrate and gallium, and the flow rates of hydrogen, hydrogen chloride, and arsine. The temperature of gallium has been maintained at 880°-890°C, and the results of many deposition experiments during the first phase of this program have concluded that the optimum substrate temperature is about 775°C and that an excess of arsine (such as an $AsH_3/HC\ell$ molar ratio of 2) should be used.

During the current reporting period, the initial stage of deposition of gallium arsenide on tungsten/graphite substrates has been investigated, and the effects of process parameters, such as the flow rate of hydrogen chloride, have been further studied.

II.1.2 Initial Stage of Deposition

The initial stage of deposition of gallium arsenide films on tungsten/graphite substrates has been investigated at 775°C by using hydrogen

chloride at a flow rate of 45 mℓ/min and an $AsH_3/HC\ell$ molar ratio of 2. The durations of deposition were 15 sec, 30 sec, 1 min, and 3 min. The deposited films were then examined by using a scanning electron microscope. The rate of nucleation and the density of nuclei appear to be rather high. Figures 2 and 3 show respectively the surface of gallium arsenide deposits after 15 and 30 seconds of deposition. About 10% of the substrate surface was covered by gallium arsenide cyrstallites after 15 seconds of deposition, and about 90% of the surface was covered after 30 seconds of deposition. In both cases, the crystallites are too small to determine if they exhibit any geometries. Figures 4 and 5 show the scanning electron micrographs of gallium arsenide films after 1 minute and 3 minutes of deposition, respectively. The gallium arsenide film is continuous after 1 minute of deposition, and the average size of crystallites is of the order of 1 μm. The crystallite size is increased to 2-3 μm after 3 minutes of deposition.

At lower flow rates of hydrogen chloride, such as 15 mℓ/min, the initial stage of deposition of gallium arsenide on tungsten/graphite substrates is similar to those shown in Figures 2 and 3. More than 90% of the substrate surface is covered by gallium arsenide crystallites after 1 minute of deposition as shown in Figure 6. Since the gallium arsenide film on tungsten/graphite substrates is continuous after a relatively short deposition time, the use of gallium arsnide/tungsten/graphite structures is a promising approach for the fabrication of thin film gallium arsenide solar cells.

II.1.3 Effect of Hydrogen Chloride Flow Rate

In most gallium arsenide deposition experiments, the temperature of gallium was maintained at 880-890°C and the flow rates of hydrogen,

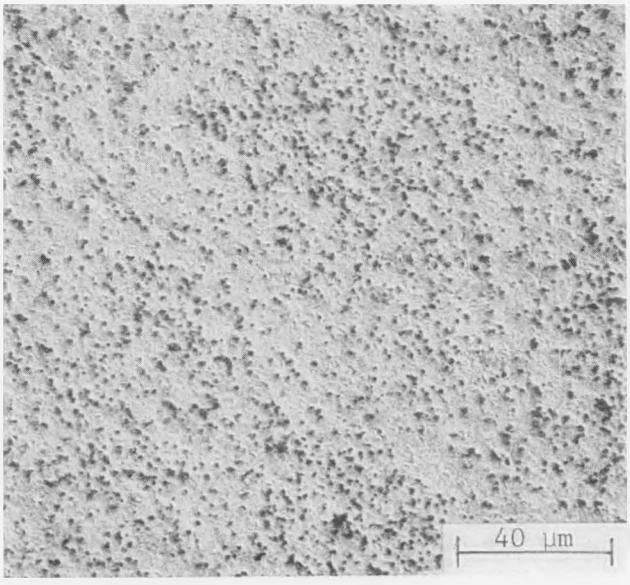


Figure 2 Scanning electron micrograph of the gallium arsenide deposit on a tungsten/graphite substrate after 15 seconds of deposition at 775°C using a hydrogen chloride flow rate of 45 mℓ/min.

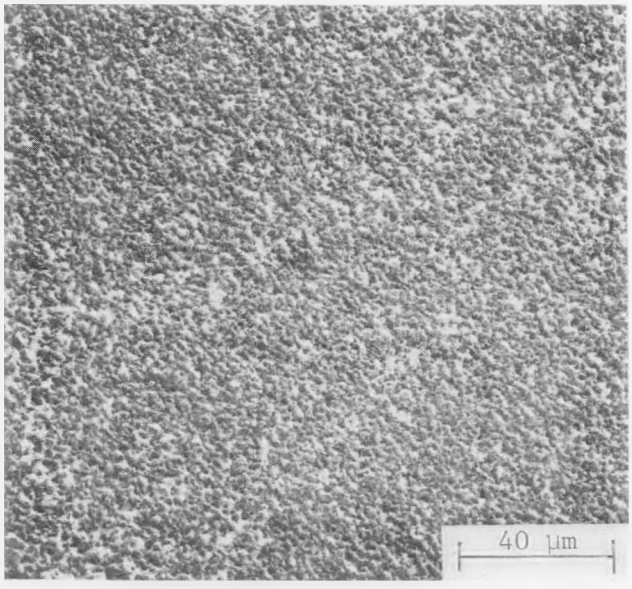


Figure 3 Scanning electron micrograph of the gallium arsenide deposit on a tungsten/graphite substrate after 30 seconds of deposition at 775°C using a hydrogen chloride flow rate of 45 mℓ/min.

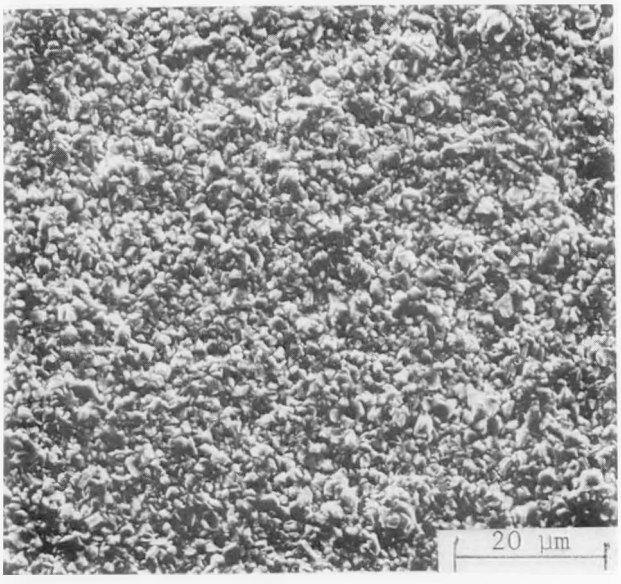


Figure 4 Scanning electron micrograph of the gallium arsenide deposit on a tungsten/graphite substrate after 1 minute of deposition at 775°C using a hydrogen chloride flow rate of 45 mℓ/min.

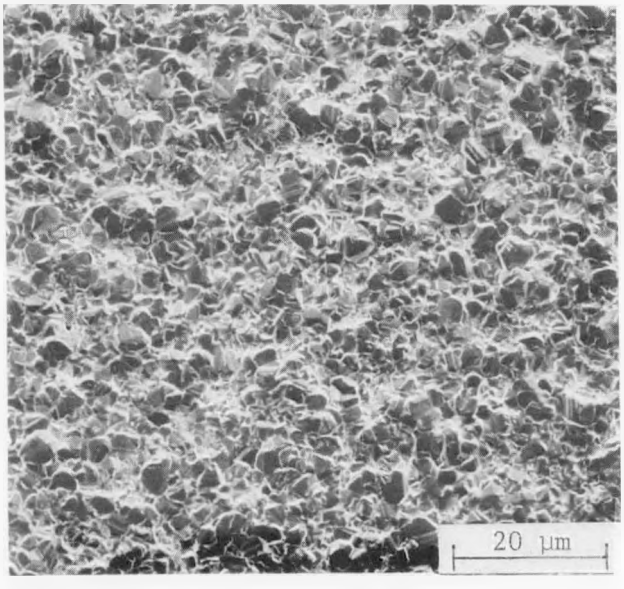


Figure 5 Scanning electron micrograph of the gallium arsenide deposit on a tungsten/graphite substrate after 3 minutes of deposition at 775°C using a hydrogen chloride flow rate of 45 mℓ/min.

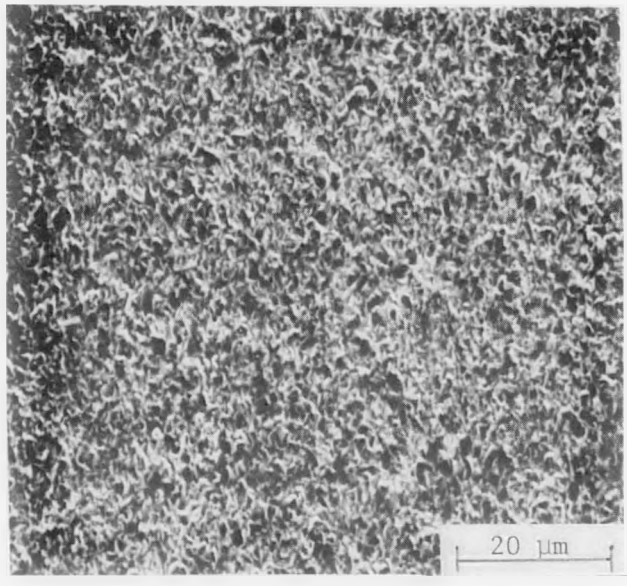


Figure 6 Scanning electron micrograph of the gallium arsenide deposit on a tungsten/graphite substrate after 1 minute of deposition at 775°C using a hydrogen chloride flow rate of 15 mℓ/min.

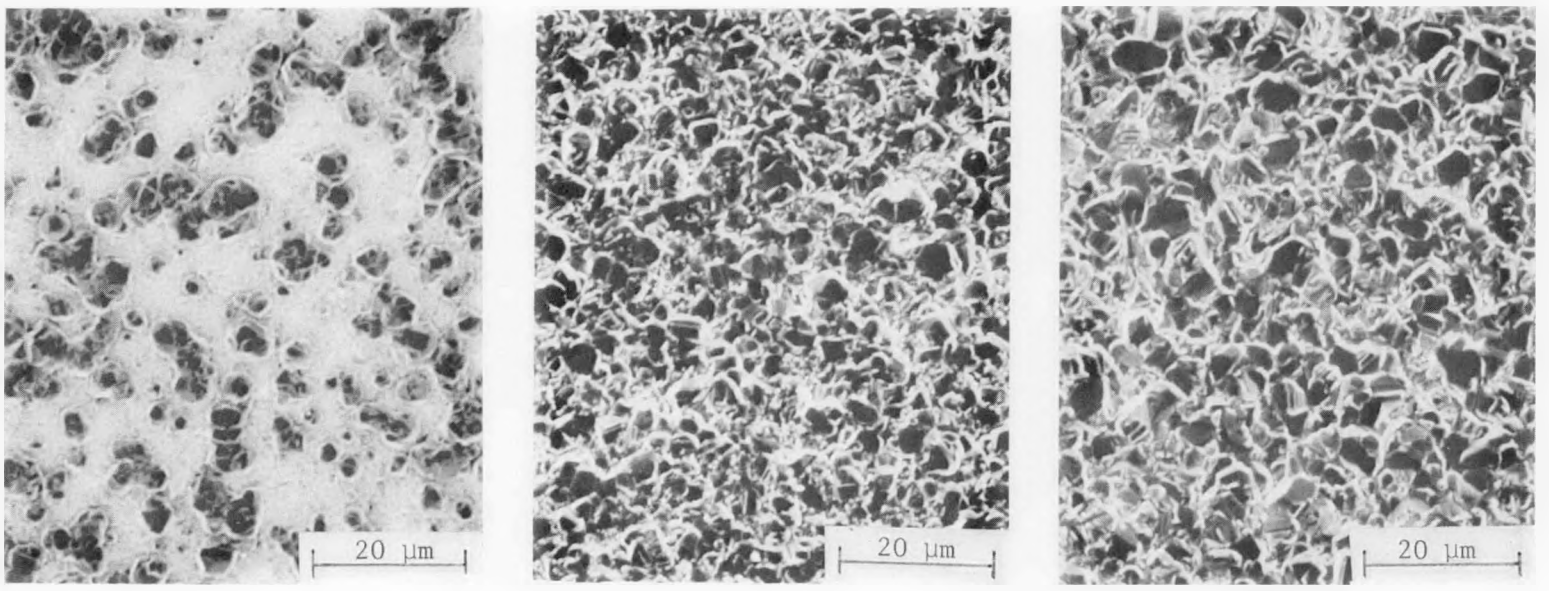
hydrogen chloride, and arsine were fixed at 1 ℓ/min, 45 mℓ/min, and 90 mℓ/min, respectively. The deposition rate and average crystallite size have been found to depend strongly on the substrate temperature. In films deposited at 775°C, the deposition rate is approximately 1.5 μm/min, and the average crystallite size is larger than 10 μm. The carrier concentrations are usually in the range of $5 \times 10^{16} - 10^{17} cm^{-3}$.

To study the effects of the concentration of hydrogen chloride in the reactant mixture, a series of experiments have been carried out using hydrogen, hydrogen chloride, and arsine at flow rates of 1 ℓ/min, 15 mℓ/min, and 30 mℓ / min, respectively (the $AsH_3/HC\ell$ molar ratio is unchanged). The average deposition rate at 775°C is 0.6-0.8 μm/min. In films of 10 - 15 μm thickness, the average crystallite size is in the range of 4 - 6 μm. X-ray diffraction examinations indicated that they are essentially polycrystalline showing no appreciable preferred orientations. The carrier concentrations in these films measured by the differential capacitance technique is in the range of $(1 - 5) \times 10^{17} cm^{-3}$, higher than that in gallium arsenide films deposited by using high flow rates of hydrogen chloride, typically $10^{16} - 10^{17} cm^{-3}$ at a hydrogen chloride flow rate of 45 mℓ/min. Thus higher dopant concentration could be related to the auto doping effect from tungsten or the more pronounced diffusion of impurities from the substrate.

II.1.4 Effects of Adding Hydrogen Chloride to Reactant Mixture

Since the deposition of gallium arsenide films by the halide process is chemically reversible, the addition of hydrogen chloride to the reactant mixture (GaCl and AsH_3) could improve the microstructure and

crystallographic properties of the deposit by reducing the rate of nucleation during the initial stage of deposition. To verify this hypothesis, a number of experiments have been carried out to deposit gallium arsenide on tungsten/graphite substrates under the usual conditions; however, varied amounts (5 mℓ/min to 40 mℓ/min) of hydrogen chloride were added to the reactant mixture. The effect of hydrogen chloride was most pronounced at a high flow rate of hydrogen chloride. When the flow rate of the additional hydrogen chloride was 40 mℓ/min, the crystallites were up to 30 - 40 μm in size after 5 minutes of deposition, however, less than 30% of the substrate surface was covered. When the flow rate of additional hydrogen chloride was reduced to 5 mℓ/min, nearly 50% of the substrate was covered after 1 minute of deposition, with crystallite size of up to 2 - 3 μm, as shown in Figure 7A. Figures 7B and 7C show the scanning electron micrographs of the gallium arsenide after 3 minutes and 5 minutes of deposition, respectively, under similar conditions. The gallium arsenide films are continuous, and the average crystallite size is 3 - 4 μm after 3 minutes of deposition and about 5 μm after 5 minutes of deposition. With the flow rate of additional hydrogen chloride increased to 10 mℓ/min, the gallium arsenide film is continuous after 5 minutes of deposition, and the average crystallite size is 6 - 7 μm, as shown in Figure 8. Figure 9 shows the scanning electron micrograph of a gallium arsenide film after 30 minutes of deposition with an additional hydrogen chloride flow rate of 20 mℓ/min. Although many crystallites are up to 100 μm in size, the crystallite size in the gallium arsenide film is not uniform with many pin holes. These results demonstrate the usefulness of using hydrogen chloride to reduce the nucleation rate of gallium arsenide on tungsten/



(A) (B) (C)

Figure 7 Scanning electron micrograph of the gallium arsenide deposits on tungsten/graphite substrate after (A) 1 minute, (B) 3 minutes, and (C) 5 minutes of deposition. Additional hydrogen chloride flow rate: 5 mℓ/min.

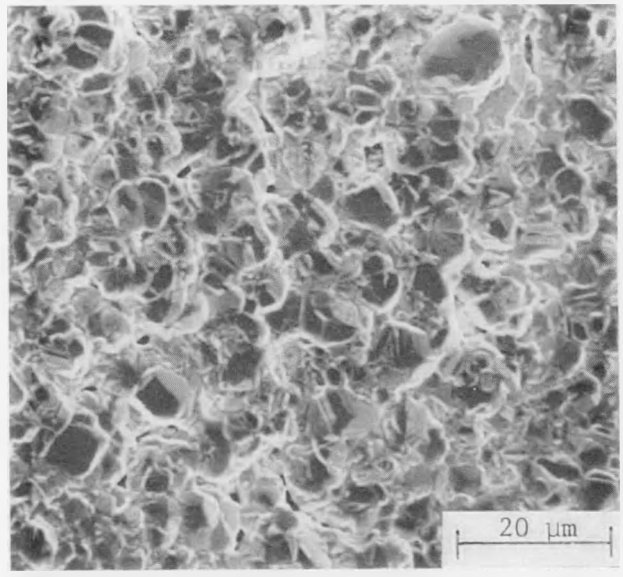


Figure 8 Scanning electron micrograph of the gallium arsenide deposit on a tungsten/graphite substrate after 5 minutes of deposition using an additional hydrogen chloride flow rate of 10 mℓ/min to the reactant mixture.

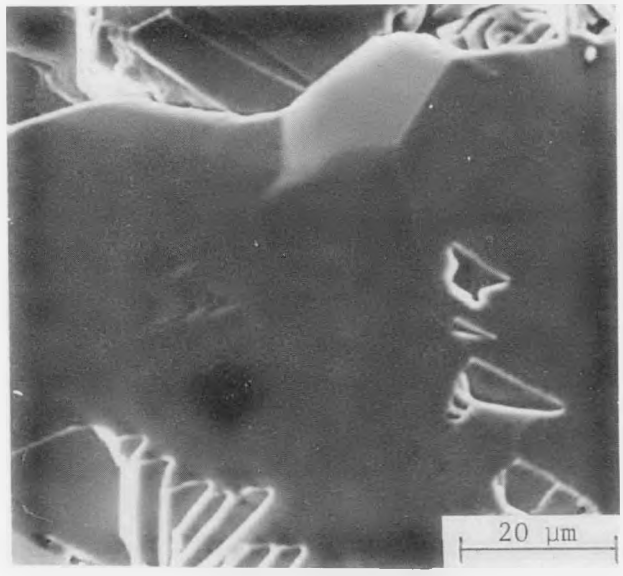


Figure 9 Scanning electron micrograph of the gallium arsnide deposit on tungsten/graphite substrate after 30 minutes of deposition using an additional hydrogen chloride flow rate of 20 mℓ/min to the reactant mixture.

graphite substrates and to improve the crystallite size in gallium arsenide films. However, further optimization is necessary to produce gallium arsenide films with uniformly large crystallites.

II.2 The Gallium-Hydrogen Chloride-Arsenic Process

Gallium arsenide films used in this program have been deposited by the reaction between gallium, hydrogen chloride, and arsine because of its simplicity and low cost. However, the impurity content in commercial arsine often varies, thus affecting the carrier concentration in deposited gallium arsenide films. To minimize these variations, the reaction between gallium, hydrogen chloride, and arsenic has been investigated for the deposition of gallium arsenide films since arsenic is readily available in purities of higher than 99.999%. The gallium-hydrogen chloride-arsenic process has been reported by others.[2] In this process, a three-zone furnace is used to maintain arsenic at about 425°C, gallium at 800-850°C, and the substrate at 750-800°C. Similar to the gallium-hydrogen chloride-arsine process, gallium is converted into gallium monochloride. Hydrogen is used as a carrier gas for arsenic. Both gallium monochloride and arsenic are carried over to the substrate surface where they react to yield gallium arsenide. The chemical reactions are:

$$2Ga(\ell) + 2HC\ell(g) \rightarrow 2GaC\ell(g) + H_2(g)$$

$$6GaC\ell(g) + As_4(g) \rightarrow 4GaAs(s) + 2GaC\ell_3(g)$$

Single crystalline gallium arsenide wafers with main faces of a {100} orientation were used as substrates for this deposition process. In these experiments, a five zone furnace is used to maintain the temperatures

of the substrates and gallium at 730-750°C and 870-890°C, respectively. The temperature of arsenic was adjusted to yield an As/Ga molar ratio of 2. The flow rate of hydrogen chloride was varied in the range of 10 - 45 mℓ/min and the flow rate of hydrogen was 1 ℓ/min. N-type epitaxial films of good structural perfection were obtained in all cases. The net carrier concentrations in gallium arsenide films are in the range of $(4 - 8) \times 10^{15} cm^{-3}$.

Tungsten coated graphite substrates were also used for the deposition of gallium arsenide films by the reaction between gallium, hydrogen chloride, and arsenic. Using hydrogen and hydrogen chloride at flow rates of 1 ℓ/min and 30 mℓ/min, respectively, and the arsenic temperature of 590°C, the deposition rate of gallium arsenide was about 0.8 - 1 μm/min, and the average crystallite size was 10 - 15 μm. The structural and electrical properties of deposited films are very similar to those of gallium arsenide films deposited from good quality arsine. Thus, the reaction between gallium, hydrogen chloride, and arsenic is also a promising method for the deposition of gallium arsenide films.

III. Chemical Vapor Deposition of Gallium Arsenide on Graphite Substrates

Graphite is a relatively economic substrate for large area gallium arsenide solar arrays for several reasons. It is compatible with gallium arsenide in properties. Several types of graphite, such as grade DFP and TRA graphite manufactured by POCO Graphite Incorporated, have thermal expansion coefficients similar to that of gallium arsenide. Graphite is chemically inert under the conditions used for the chemical vapor deposition of gallium arsenide. Furthermore, graphite has high thermal and electrical conductivities and may be used as an ohmic contact to the solar cell. However, n-gallium arsenide/graphite structures have been found to exhibit rectifying characteristics, and a tungsten interlayer has been used to provide an ohmic contact to gallium arsenide. The processing of solar cells can be simplified if the tungsten interlayer could be eliminated. This is also desirable since the thermal expansion coefficient of tungsten is smaller than that of gallium arsenide or graphite. The feasibility of using a heavily-doped gallium arsenide layer in place of the tungsten interlayer for solar cell purposes has been investigated.

III.1 Deposition of Gallium Arsenide Films

The deposition of gallium arsenide films on graphite substrates was carried out by the reaction of gallium, hydrogen chloride, and arsine in a gas flow system using the apparatus shown in Figure 1. A hydrogen-hydrogen sulfide mixture was used as the dopant. The fused silica reaction tube was of 55 mm ID and was heated by a four zone furnace. Grade DFP and TRA graphite plates of about 1.2 mm thickness were used as the

substrates. They were heated in a hydrogen atmosphere at 1200°C for at least 0.5 hr. before the deposition of gallium arsenide films. The important process parameters in the deposition process are the temperatures of the gallium source and the substrate, and the composition and flow rate of the reactant mixture. In the deposition experiments; the temperature of gallium was maintained at 880-890°C, and the flow rates of hydrogen, hydrogen chloride, and arsine were 1 ℓ/min, 15-45 mℓ/min, and 30-90 mℓ/min, respectively (the use of an excess of arsine was to minimize any arsenic deficiency in the deposit). The substrate temperature and the $H_2S/HC\ell$ molar ratio were varied in the range of 725-825°C and $1.7 \times 10^{-4} - 10^{-2}$, respectively. The thickness of deposited gallium arsenide films was determined by direct measurement on vertical cross-sectioned surface.

III.2 Initial Stage of Deposition

The initial nucleation of gallium arsenide on graphite substrates is quite different from that on tungsten/graphite substrates shown in Figs. 2 and 3. Under the same deposition conditions, the rate of nucleation of gallium arsenide on graphite substrates is considerably lower than that on tungsten/graphite substrates. This is illustrated in Figure 10A where the duration of deposition was 1 minute. The deposit consists of many islands of relatively large crystallites, and the non-uniform deposition is presumably due to the inhomogeneous surface associated with the porosity of graphite (about 20%). The deposit is essentially continuous after 3 minutes of deposition. Figure 10B shows the surface of a gallium arsenide film on a graphite substrate after 5 minutes of deposition, where the average crystallite size is about 5 μm.

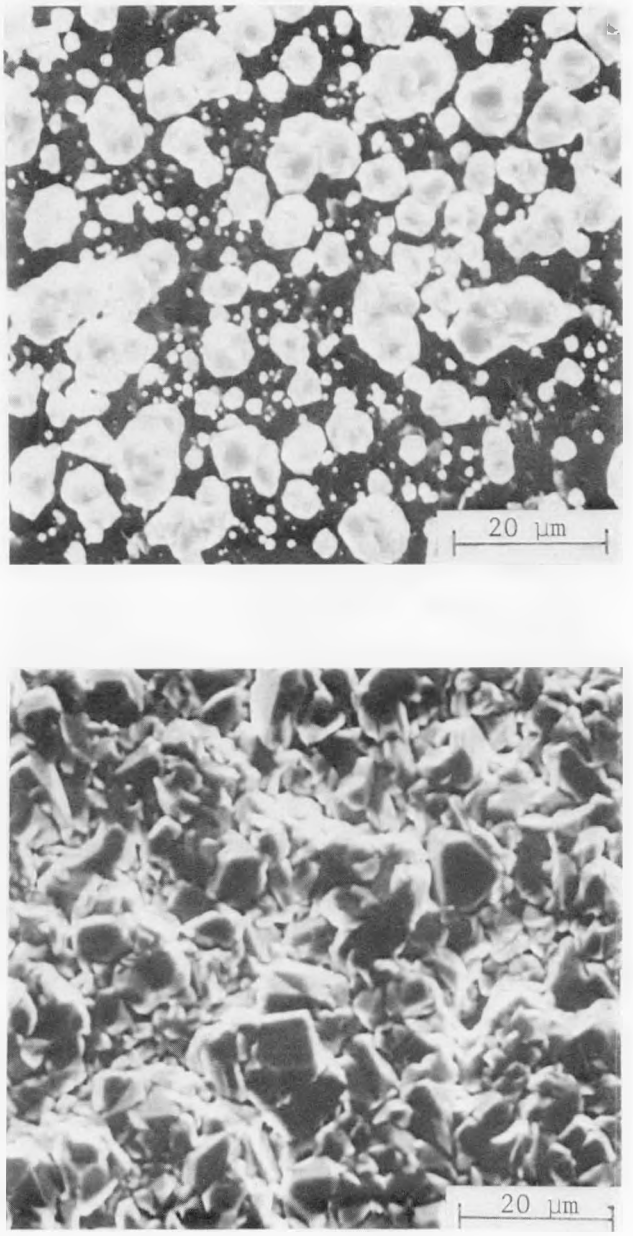


Figure 10 Scanning electron micrograph of the gallium arsenide deposit on a graphite substrate after (A) 1 minute and (B) 5 minutes of deposition at 775°C using a hydrogen chloride flow rate of 45 mℓ/min.

III.3 Structural Properties

A series of experiments have been carried out to determine the effects of substrate temperature and reactant composition on the structural properties of gallium arsenide films deposited on graphite substrates. The substrate temperature was in the range of 725-825°C, and the flow rate of hydrogen chloride was in the range of 15-45 mℓ/min. Preliminary results indicate that by using a hydrogen chloride flow rate of 15 mℓ/min and an $AsH_3/HC\ell$ molar ratio of 2, the average size of crystallites increases with decreasing substrate temperature. For example, the average crystallite size in gallium arsenide films of 20 μm thickness deposited at 725°C is about 8 μm and that in films of 15 μm thickness deposited at 775°C is about 4 μm. Figures 11 and 12 show the scanning electron micrograph of the surface of gallium arsenide films deposited at 725° and 775°C, respectively. At high flow rates of hydrogen chloride, such as 45 mℓ/min, the size of gallium arsenide crystallites becomes more non-uniform, although relatively large crystallites are frequently present. Figure 13 shows the surface of a gallium arsenide film of about 30 μm thickness deposited on a graphite substrate at 775°C by using a hydrogen chloride flow rate of 45 mℓ/min, where several crystallites are as large as 20 μm and have well developed faces. Both the deposition rate and crystallite size are not affected appreciably by the incorporation of sulfur in the concentration range under study.

The crystallographic properties of gallium arsenide films deposited on graphite substrates were examined by the X-ray diffraction technique using CuK_α radiation. Polycrystalline gallium arsenide of random orientations is known to show three strong diffraction peaks associated with

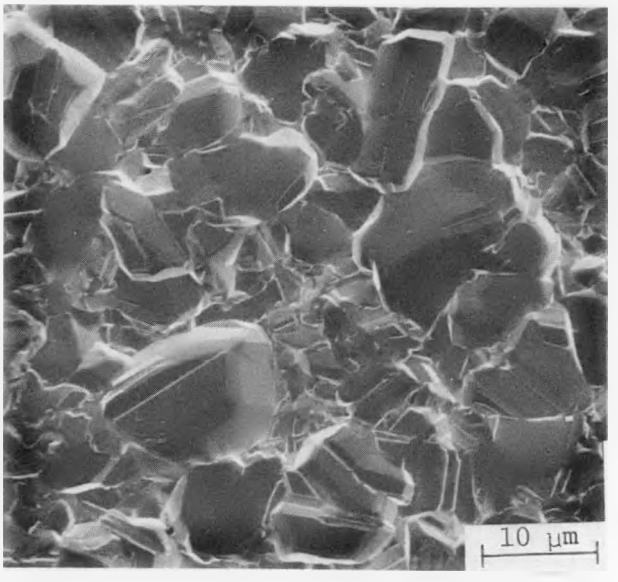


Figure 11 Scanning electron micrograph of the surface of a gallium arsenide film deposited on a graphite substrate at 725°C using hydrogen, hydrogen chloride, and arsine at flow rates of 1 ℓ/min, 15 mℓ/min, and 30 mℓ/min, respectively. Deposition time: 30 minutes.

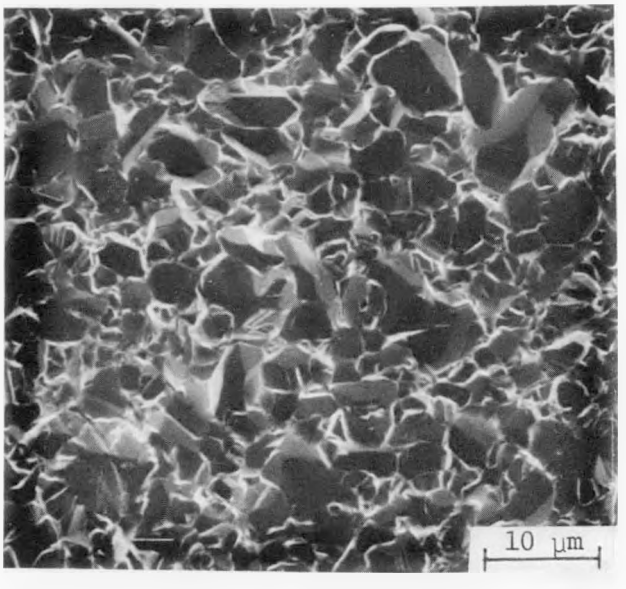


Figure 12 Scanning electron micrograph of the surface of a gallium arsenide film deposited on a graphite substrate at 775°C under the same conditions as those in Figure 11. Deposition time: 30 minutes.

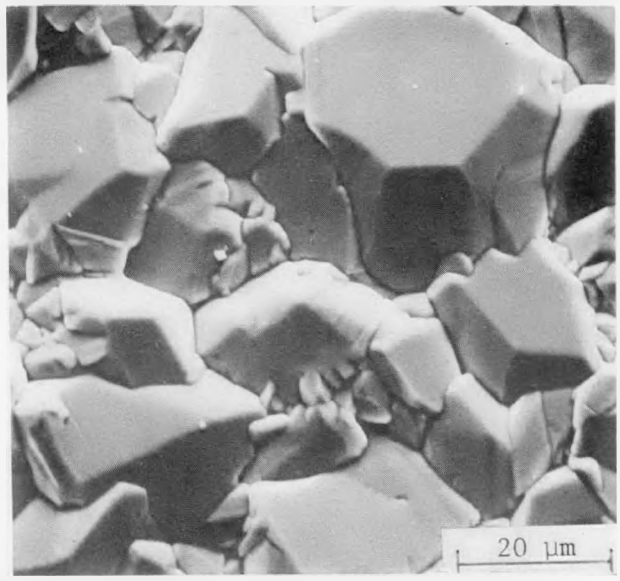


Figure 13 Scanning electron micrograph of the surface of a gallium arsenide film deposited on a graphite substrate at 775°C using hydrogen, hydrogen chloride, and arsine at flow rates of 1 ℓ/min, 45 mℓ/min, and 90 mℓ/min, respectively. Deposition time: 30 minutes.

{111}, {220}, and {311} reflections with 2θ values of 27.3°, 45.3°, and 53.8° and relative intensities of 100, 35, and 35.[6] The diffraction spectra of the gallium arsenide films were obtained by scanning 2θ in the range of 20-60°. The relative intensities of {111}, {220}, and {311} reflections were found to be independent of the substrate temperature and to depend only slightly on the dopant concentration. Figures 14A and 14B show the diffraction spectra of gallium arsenide films deposited at 775°C by using $H_2S/HC\ell$ molar ratios of 10^{-2} and 1.7×10^{-4}, respectively. While the film with the low dopant concentration shows a weak {111} preferred orientation, the film with the high dopant concentration is essentially polycrystalline.

III.4 Electrical Properties of n^+-GaAs/ Graphite Structures

Attempts were made to determine the carrier concentrations in sulfur-doped gallium arsenide films on graphite substrates by the differential capacitance method. An array of silver dots of about 0.5 mm diameter were evaporated onto each gallium arsenide film through a metal mask. However, the capacitance of these Schottky barriers cannot be measured as a function of reverse bias due either to the rectifying characteristics of the gallium arsenide/graphite interface or the high conductivity of the Schottky barrier structures.

The dark current-voltage characteristics of the silver/gallium arsenide/graphite structures were first measured at room temperature and were remeasured after heat treatment in a hydrogen atmosphere at 450°C for 0.5 hr. The heat treatment would, in most cases, make the Ag/GaAs interface ohmic; however, the characteristics of the GaAs/graphite

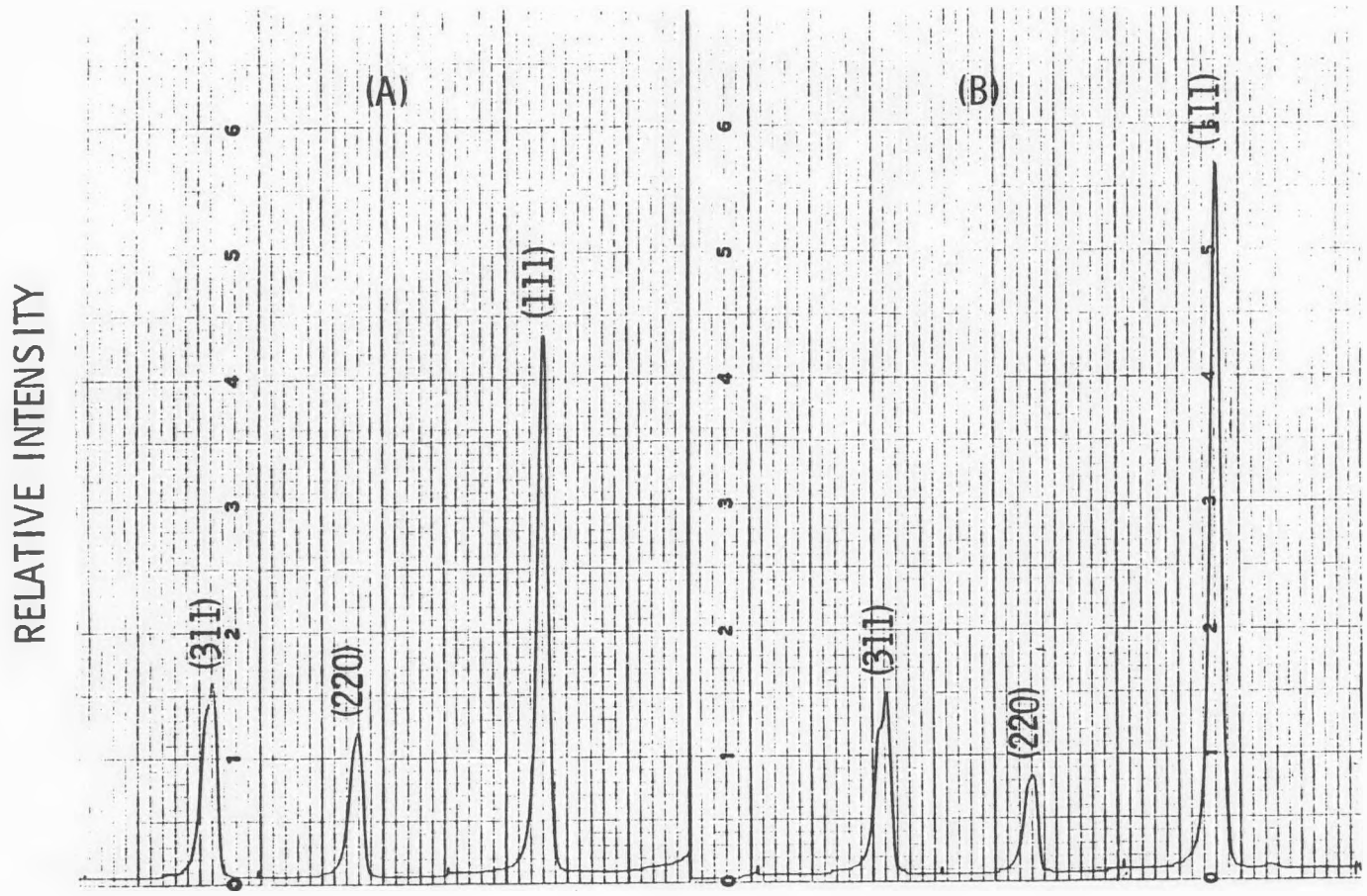


Figure 14 X-ray diffraction spectra of gallium arsenide films deposited on graphite substrates at 775°C by using (A) a $H_2S/HC\ell$ molar ratio of 10^{-2}, and (B) a $H_2S/HC\ell$ molar ratio of 1.7×10^{-4}.

interface should remain unchanged since the deposition of gallium arsenide was carried out at temperatures considerably higher than the heat treatment temperature.

The characteristics of silver/gallium arsenide/graphite structures with gallium arsenide deposited at 775°C are discussed here in some detail. Figure 15 shows the typical characteristics of a structure prepared with a $H_2S/HC\ell$ molar ratio of 1.7×10^{-4} before and after heat treatment; the solid lines represent the characteristics when the silver contact is positive with respect to graphite, and the dotted lines represent the characteristics where the silver contact is negative. When the silver contact is positive, the Ag/GaAs interface is forward biased, and the GaAs/graphite interface is reverse biased. Thus, these characteristics are essentially unchanged after heat treatment, and the GaAs/graphite interface has a relatively high impedance. When the silver contact is negative, however, the Ag/GaAs interface is reverse biased, and the measured characteristics are dominated by this interface. Upon heat treatment, the Ag/GaAs barrier height is lowered, and the Ag/GaAs/graphite structure exhibits considerably lower impedance. When such a structure is used for solar cell purposes, one may estimate the series resistance from the characteristics measured with silver positive. For example, at a current density of 20 mA/cm^2, the voltage drop across the structure would be 200-220 mV, indicating an excessive series resistance. The GaAs/graphite interface resistance and thus the voltage drop across the Ag/GaAs/graphite structure can be reduced by increasing the dopant concentration in gallium arsenide. When the $H_2S/HC\ell$ molar ratio in the reactant mixture for the deposition of gallium arsenide was increased to 5×10^{-4}, the voltage

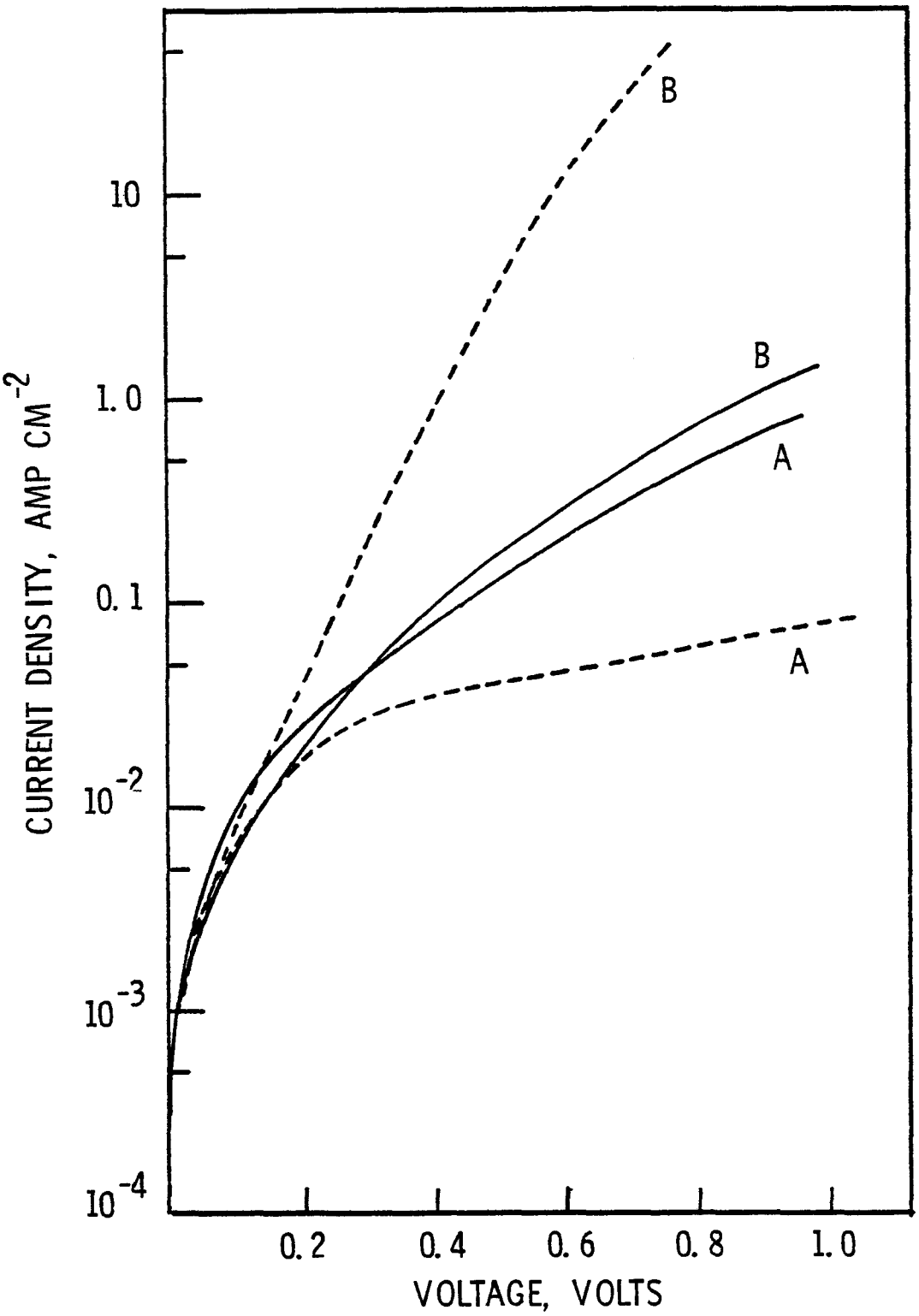


Figure 15. The current-voltage characteristics of a Ag/GaAs/graphite structure, prepared at 775°C using a $H_2S/HC\ell$ molar ratio of 1.7×10^{-4}, before (A) and after (B) heat treatment. Solid lines: silver positive; dotted lines: silver negative.

drop across the Ag/GaAs/graphite structure at a current density of 20 mA/cm^2 was reduced to 150-170 mV. This voltage drop was further reduced by increasing the dopant concentration in gallium arsenide. By using H_2S/HCℓ molar ratio of 1×10^{-2}, the voltage drops across the Ag/GaAs/graphite structures at a current density of 20 mA/cm^2 have been found to be 2-3 mV (Fig. 16). Although the GaAs/graphite interface still does not exhibit ohmic behavior, a 2-3 mV drop across a solar cell at a current density of 20 mA/cm^2 is tolerable. Therefore, graphite may be used as a substrate for the direct deposition of solar cell structures.

Silver/gallium arsenide/graphite structures prepared at 725°C have higher impedance than those prepared at 775°C with the same H_2S/HCℓ molar ratio in the reactant mixture. At 725°C, for example, the voltage drops across Ag/GaAs/graphite structures under forward bias at a current density of 20 mA/cm^2 have been found to be 60-70 and 10 mV for H_2S/HCℓ molar ratios of 3.3×10^{-3} and 10^{-2}, respectively, as compared with 40-50 and 2-3 mV for gallium arsenide films deposited at 775°C with the same reactant composition.

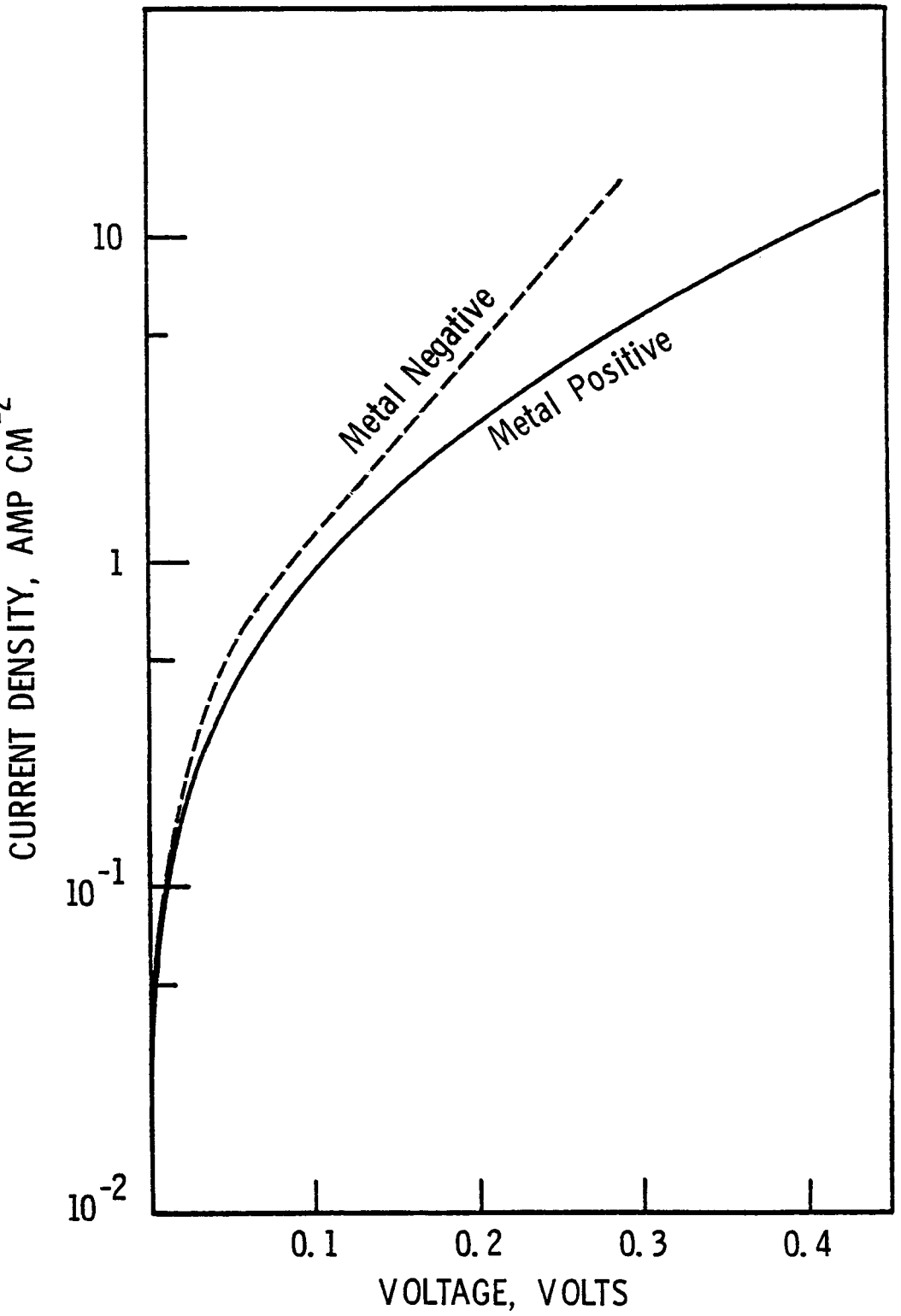


Figure 16 The current-voltage characteristics of a Ag/GaAs/graphite structure, prepared at 775°C using a $H_2S/HC\ell$ molar ratio of 1.0×10^{-2}, after heat treatment.

IV. Thin Film Gallium Arsenide MOS Solar Cells

The MOS approach was selected for the fabrication of thin film gallium arsenide solar cells. This approach is advantageous over the use of p-n homojunctions. For example, the surface recombination of photogenerated carriers, a serious problem in p-n homojunctions, is negligible in the MOS cells. The MOS devices are formed at relatively low temperature, eliminating the effects of rapid dopant diffusion along grain boundaries. The use of an oxide interlayer serves two purposes: (1) to increase the metal-gallium arsenide barrier height and thus the voltage output, and (2) to reduce the shunting effects of grain boundaries. The fabrication and characteristics of MOS solar cells on graphite and tungsten/graphite substrates, including the deposition of anti-reflection coatings, are discussed in this section.

IV.1 Titanium Dioxide Films as Antireflection Coatings

The antireflective coating is an important parameter in the design and fabrication of solar cells.[7,8] Since gallium arsenide has relatively high refractive indices, about 3.6 at 900 nm and 4.8 at 450 nm at room temperature, more than 30% of the incident light is lost by reflection, and coatings of appropriate refractive index and thickness must be applied to reduce this loss. The optical thickness of the coating should be one-quarter wavelength at wavelength near the peak of the cell response-solar output product curve. The optimum refractive index of the coating to give zero reflectance at the quarter-wavelength thickness is $(n_1 n_2)^{\frac{1}{2}}$, where n_1 and n_2 are the refractive indices of the semiconductor

and the medium surrounding the antireflection coating, respectively. Thus, the optimum refractive index of coatings should be about 2 for uncovered cells and about 2.5 for cells with glass covers (refractive index 1.5).

The selection of antireflection coatings for MOS solar cells are especially important since the metal films on the semiconductor surface greatly increases the solar reflectance. For example, for 100 Å metal films on gallium arsenide, reflection is the biggest optical loss, amounting to about 35% for the most transparent films such as copper, gold, or silver.[9] Films of several oxides, such as antimony trioxide, niobium pentoxide, tantalum pentoxide, titanium dioxide, etc., are suitable as antireflection coatings for thin film gallium arsenide MOS solar cells. Titanium dioxide is particularly attractive because of the ease of application at relatively low temperatures. Hovel has recently reported the use of the hydrolysis of tetraisopropyl titanate by a spray process in air for the deposition of titanium oxide films on gallium arsenide p-n junction and Schottky barrier solar cells at relatively low temperatures, 60° or above.[10] The deposition rate was 2-10 Å/sec; the films deposited at temperatures below 200°C were found to be amorphous, and a transformation to a polycrystalline phase was observed at 200°-300°C. The optical properties of sprayed titanium dioxide films depend strongly on the deposition temperature. For example, the refractive index (measured with a He-Ne laser at 6238 Å) is about 1.9 for temperatures below 100°C, increases linearly between 120° and 340°C, and saturates at about 2.4 at 400°C. The refractive index of films deposited at all temperatures increases strongly at short wavelengths. The optical

absorption was least for films deposited at the lowest temperature. The absorption edge shifts to longer wavelengths with increasing deposition temperatures up to 200°C, reverts to a shorter wavelength between 200° and 240°C, and then continues its shift to longer wavelengths.

Titanium dioxide films used as antireflection coatings for thin film gallium arsenide MOS cells in this work have been prepared by the hydrolysis of tetraisopropyl titanate in a gas flow system. Since tetraisopropyl titanate hydrolyzes readily, the experimental conditions must be controlled so that the reaction is predominately heterogeneous taking place on the substrate surface. Otherwise, reactions in the volume surrounding the substrate can yield solid products in the gas phase, and the deposition of these solids on the substrate would yield nonadherent material. The volume reaction can be suppressed by using a low partial pressure of the reactants in the reaction chamber and a high linear velocity of the gas mixture over the substrate surface. An apparatus for the deposition of titanium dioxide films has been constructed and is shown schematically in Figure 17. It consists of two parts: the gas flow control and the reaction tube. The solar cells are supported on a graphite susceptor in a fused silica reaction tube. The susceptor is heated externally by an rf generator, and its temperature is monitored by a thermocouple inserted into the susceptor. The tetraisopropyl titanate container is also placed in the reaction tube and its vapor is carried over to the substrate surface by argon. Argon is also used as a carrier gas to introduce water vapor to the substrate surface. It is important that the mixing of tetraisopropyl titanate and water vapor take place on the surface of the substrate to minimize homogeneous nucleations.

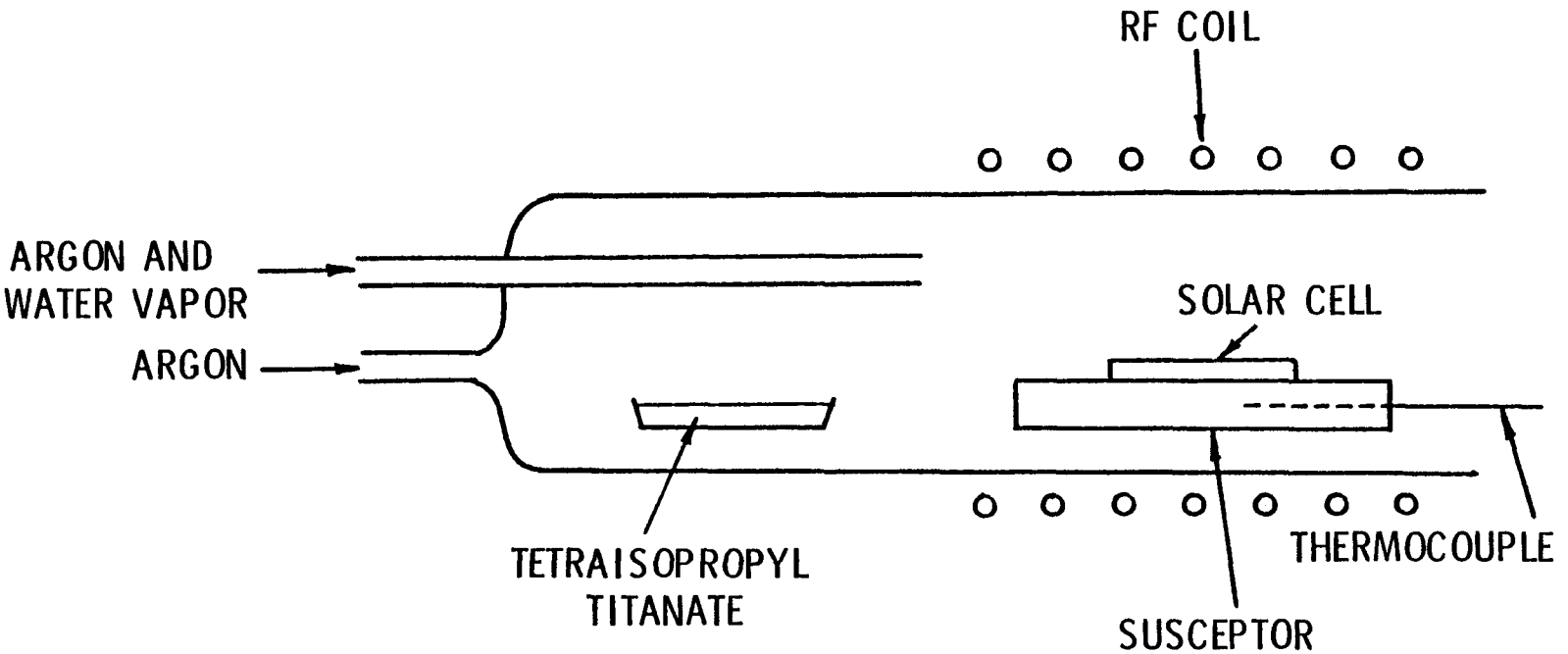


Figure 17 Schematic diagram of the apparatus for the deposition of titanium dioxide films.

A number of experiments have been carried out using argon flow rate in the range of 2-10 ℓ/min, solar cell temperature at 60-100°C, and sufficient tetraisopropyl titanate and water vapor to yield deposition rates of 50 Å - 500 Å/min. The deposited film is not uniform, and many attempts to improve the uniformity and reproducibility of titanium dioxide films by using different configurations of reactant tubes have not been completely successful. Also, water vapor is sometimes trapped at the interface, resulting in electrical instability of the solar cell. It is concluded that further optimization of the deposition of titanium dioxide films with the present system is difficult and that alternative approaches, such as ion-beam evaporation, should be investigated.

IV.2 Fabrication and Characterization Techniques

Many MOS solar cells have been fabricated from gallium arsenide films deposited on tungsten/graphite and graphite substrates and have been characterized by current-voltage, spectral response, diffusion length, and barrier height measurements. Strong emphasis has been directed to the control of the oxidation of gallium arsenide films. The techniques used at present are described below.

IV.2.1 Solar Cell Fabrication

The solar cells developed in this program are of the configuration TiO_2/Au(or Ag)/oxide/n-GaAs(carrier concentration: $\leq 10^{17} cm^{-3}$)/n^+-GaAs (carrier concentration: $> 10^{18} cm^{-3}$)/substrate. The deposition of gallium arsenide films was carried out at 775°C by using hydrogen, hydrogen chloride, and arsine at flow rates of 1 ℓ/min, 45 mℓ/min, and 90 mℓ/min, respectively. During the initial stage of deposition, hydrogen sulfide was

used as a dopant to yield a carrier concentration of higher than $10^{18} cm^{-3}$ in the deposited gallium arsenide. The deposition was continued without the dopant; the carrier concentration in the deposit was in the range of 5×10^{16} to $10^{17} cm^{-3}$, and no attempts were made to control this carrier concentration. Subsequent to the deposition process, gallium arsenide films were oxidized in situ with oxygen at 200°C for 0.5 - 1 hour. This in-situ oxidation assures the formation of a uniform continuous oxide film. The specimen was then transferred, with minimum exposure to air, to a glass tube maintained at 30°C through which flowed oxygen saturated with water vapor at 30°C at a rate of 100 mℓ/min. The temperatures of the reactant mixture and gallium arsenide films were controlled to within 0.5°C to obtain reproducible results. The duration of this oxidation was 8-15 hours and was optimized with respect to the solar cell characteristics; an excessive oxide thickness reduces the current output and increases the series resistance, and insufficient oxidation results in high leakage current and low voltage output.

Following the oxidation process, a gold or silver film of 60-80 Å thickness was evaporated onto the surface under a pressure of less than 10^{-6} Torr, and the grid contact was formed by the evaporation of silver through a metal mask. In addition, silver dots of about 0.5 mm diameter were also evaporated onto the surface of gallium arsenide for the measurement of carrier concentration by the differential capacitance method.

When silver is used as the barrier metal, it is essential to minimize the exposure of the device in air. Otherwise, the silver film changes to a dark color, due presumably to the formation of silver sulfide at the barrier surface, reducing the light transmission. The barrier

surface may be protected by the application of titanium dioxide anti-reflection coating. The titanium oxide film, 600-700 Å in thickness, was deposited at 80-100°C by the hydrolysis of tetraisopropyl titanate.

IV.2.2 Characterization Techniques

The properties of thin film gallium arsenide MOS solar cells were characterized by the dark current-voltage, illuminated current-voltage, spectral response, and capacitance-voltage measurements.

The dark current-voltage measurements were carried out between the grid contact and graphite by the four-probe technique. The voltage across the solar cell and the current through the cell were measured with Keithley digital multimeters. Five measurements were made for each decade of current. At any given current, the voltage was ususally reproducible within $\pm$ 0.5 mV.

The illuminated current-voltage measurements were carried out at 28°C with G.E. ELH quartz-halogen lamps calibrated with a standard silicon solar cell. The illuminated characteristics under AM1 conditions were used to calculate the conversion efficiency, and the characteristics under different levels of illumination were used to determine the series resistance of the cell.

The spectral response of each solar cell was measured at 28°C by using a single crystalline silicon solar cell with known spectral response as a reference. One 300 W GE ELH quartz-halogen lamp and interference filters for wavelengths 0.4, 0.45, 0.5, 0.6, 0.7, 0.75, 0.8, 0.85, 0.9 and 0.95 μm were used as the light source. The short circuit currents of the test cell and the reference cell were measured simultaneously at each wavelength. The spectral response of the test cell, in terms of the

short-circuit current per unit of monochromatic input power incident on a unit area of the cell, was then calculated. The spectral response of this solar cell was also used for the determination of minority carrier diffusion length in gallium arsenide films. The ratio of the measured responses at two wavelengths, 7000 and 7500 Å for example, was compared with the ratios calculated as a function of diffusion length for materials of the same dopant concentration, and the effective diffusion length in gallium arsenide films can be deduced.

The capacitance of each 0.5 mm diameter diode on the solar cell was measured as a function of reverse bias. The slope of the $1/C^2$ versus V plot was used to determine the carrier concentration and the intercept of the plot was used to calculate the barrier height. The barrier height in solar cells was also measured by the photoresponse technique using the surface photovoltage apparatus for silicon solar cells. The photoresponse of the cell was measured in the range of 10,000 and 11,500 Å, and a plot of the square root of photoresponse versus photon energy relation is used to extrapolate the barrier height.

IV.3 Results and Discussion

More than two hundred MOS solar cells have been prepared from gallium arsenide films deposited on tungsten/graphite and graphite substrates during the past year. In all cases, the metal barrier was of 9 cm^2 in area, and the grid contact, 10 lines per cm, occupy about 5% of the total area. At present, the AM1 efficiency of solar cells on tungsten/graphite substrates is about 6.5%, and that on graphite substrates is about 6%. Some typical results are discussed below.

The dark current-voltage characteristics of a typical thin film gallium arsenide gold-barrier solar cell on a tungsten/graphite substrate of 9 cm^2 area is shown in Figure 18. The diode quality factor "n" deduced from the forward characteristics is about 2.3, and the reverse current density at 0.5 V is about 10^{-6} A/cm^2. These characteristics are reasonable for a large area thin film device. The illuminated characteristics of this cell under AM1 conditions is shown in Figure 19, where the open-circuit voltage, short-circuit current density, and fill factor are 0.51 V, 22 mA/cm^2, and 59%, respectively, corresponding to a conversion efficiency of 6.7%. The series resistance of the solar cell is approximately 0.3 ohms. The conversion efficiency of silver barrier cells is similar to that of gold barrier cells except that the silver barrier cells have somewhat higher open-circuit voltage and lower short-circuit current density.

The spectral response of a typical gold-barrier cell is shown in Figure 20; the response peaks at 0.6 - 0.7 μm with an external quantum efficiency of 60-70%. The spectral response of solar cells was also used for the determination of minority carrier diffusion length in gallium arsenide films. The ratio of the measured responses at two wavelengths, 7000 and 7500 Å for example, was compared with the ratios calculated as a function of diffusion length for materials of the same dopant concentration.[11] The effective diffusion length in most gallium arsenide films was found to be in the range of 0.5 - 0.8 μm.

A typical example of the capacitance-voltage relation of a silver diode on a gallium arsenide film used for solar cells is shown in Figure 21. The carrier concentration in the gallium arsenide film calculated from the slope of the linear relation is about $5 \times 10^{16} cm^{-3}$, and the

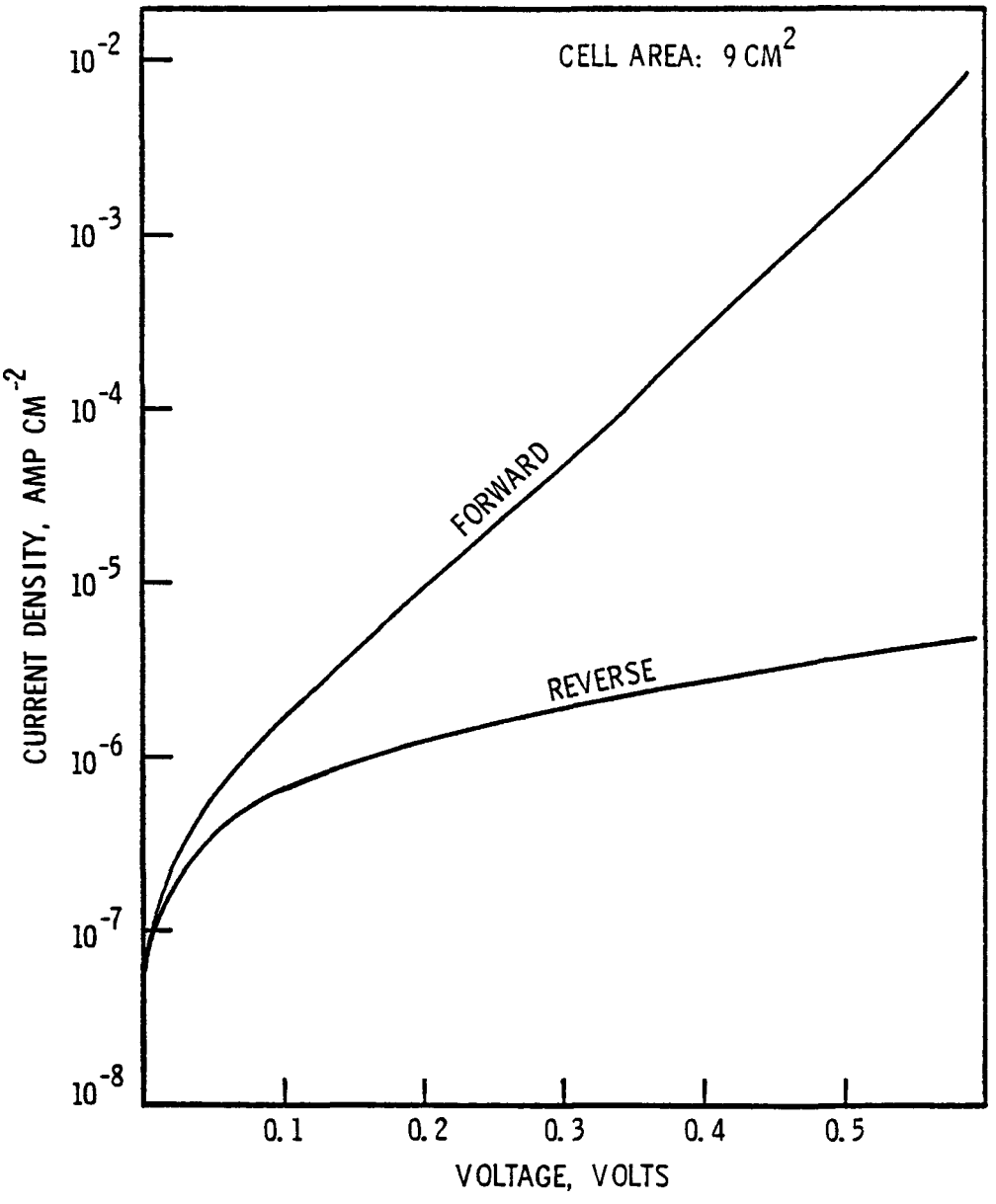


Figure 18 Dark current-voltage characteristics of a TiO_2/Au/oxide/n-GaAs/n^+-GaAs/W/graphite solar cell of 9 cm^2 area at room temperature.

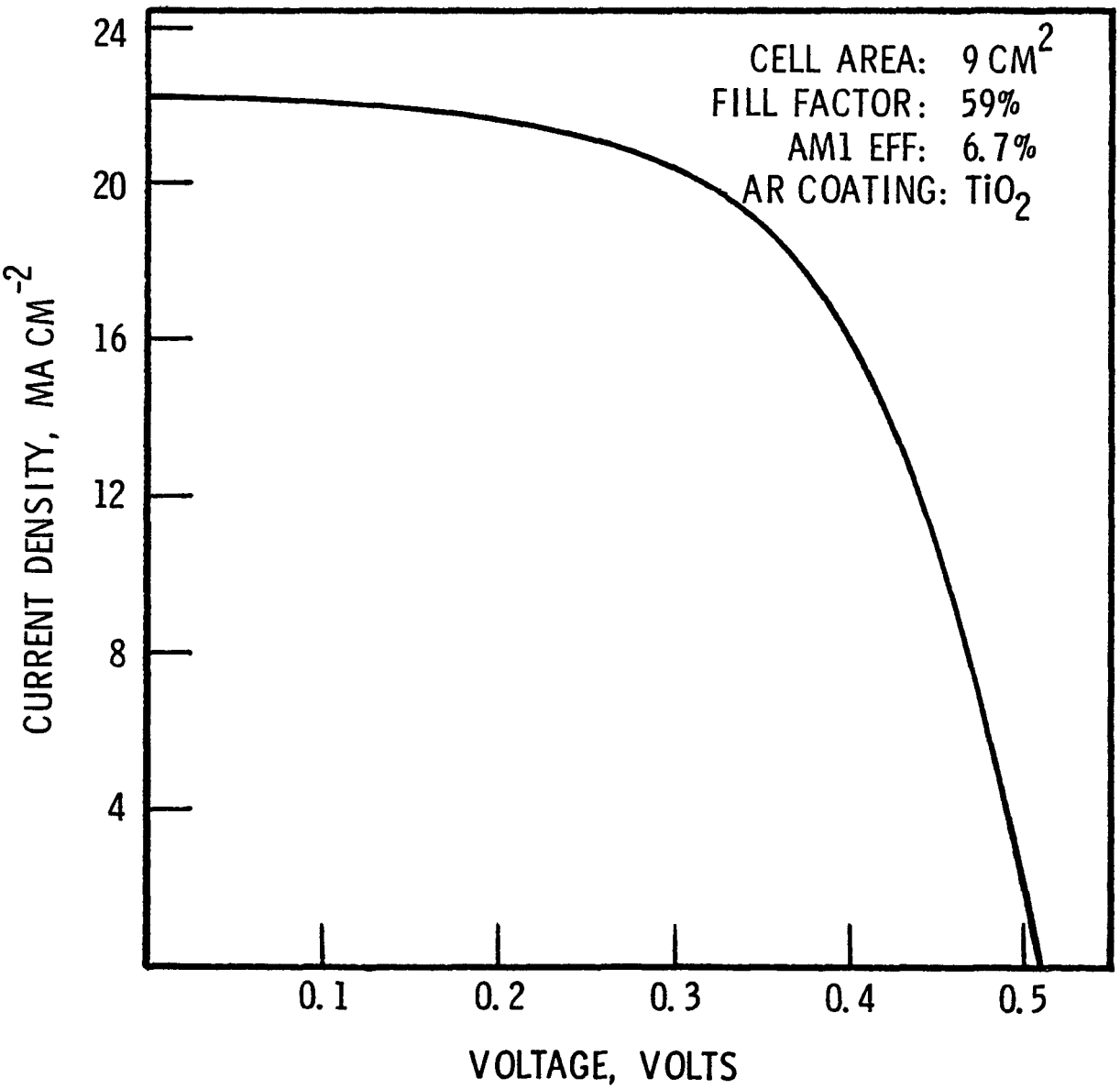


Figure 19 Current-voltage characteristics of a TiO_2/Au/oxide/n-GaAs/n^+-GaAs/W/graphite solar cell under illumination with ELH quartz-halogen lamps at AM1 conditions.

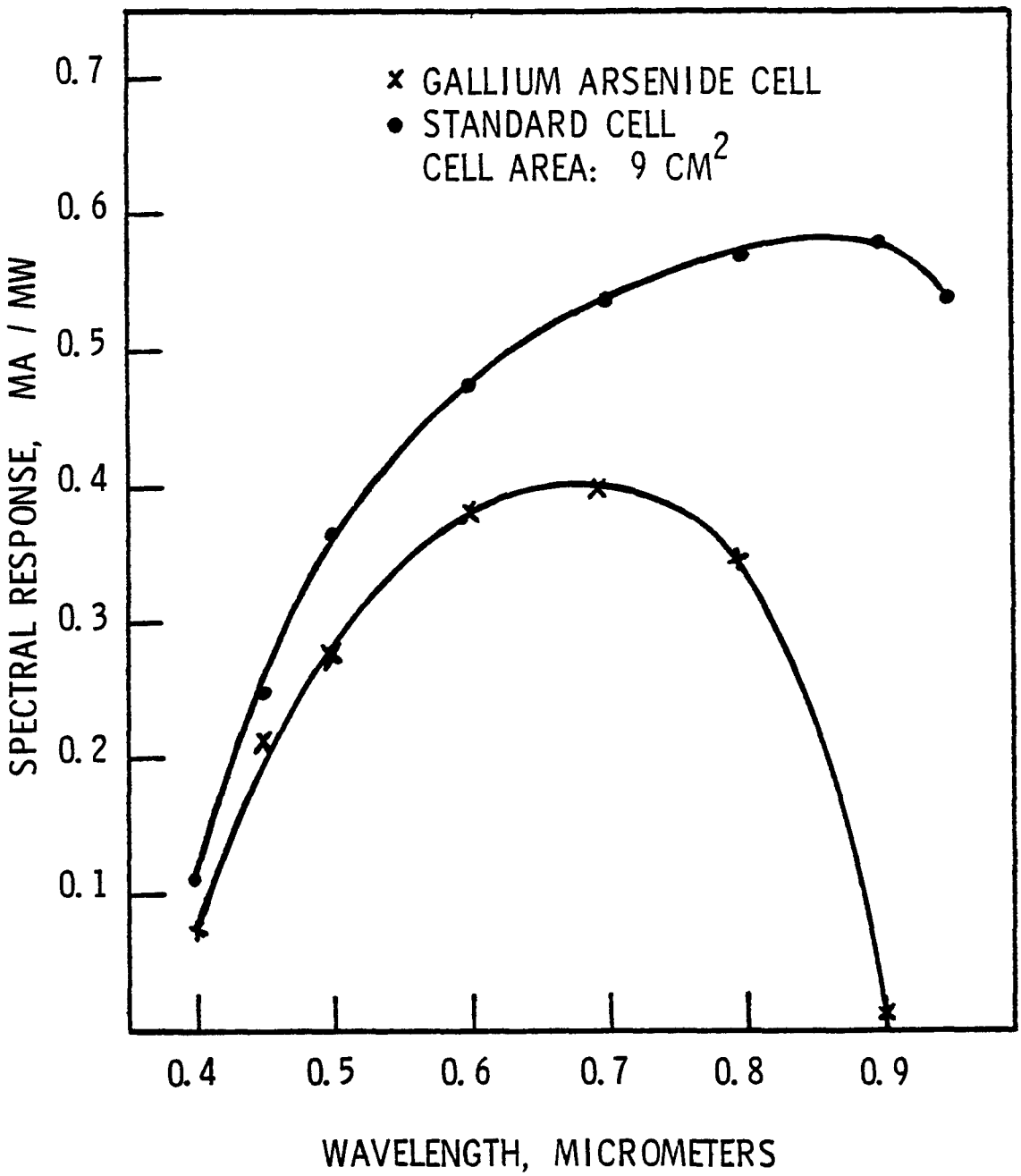


Figure 20 The spectral response of the solar cell shown in Figure 19 in comparison with a standard silicon solar cell.

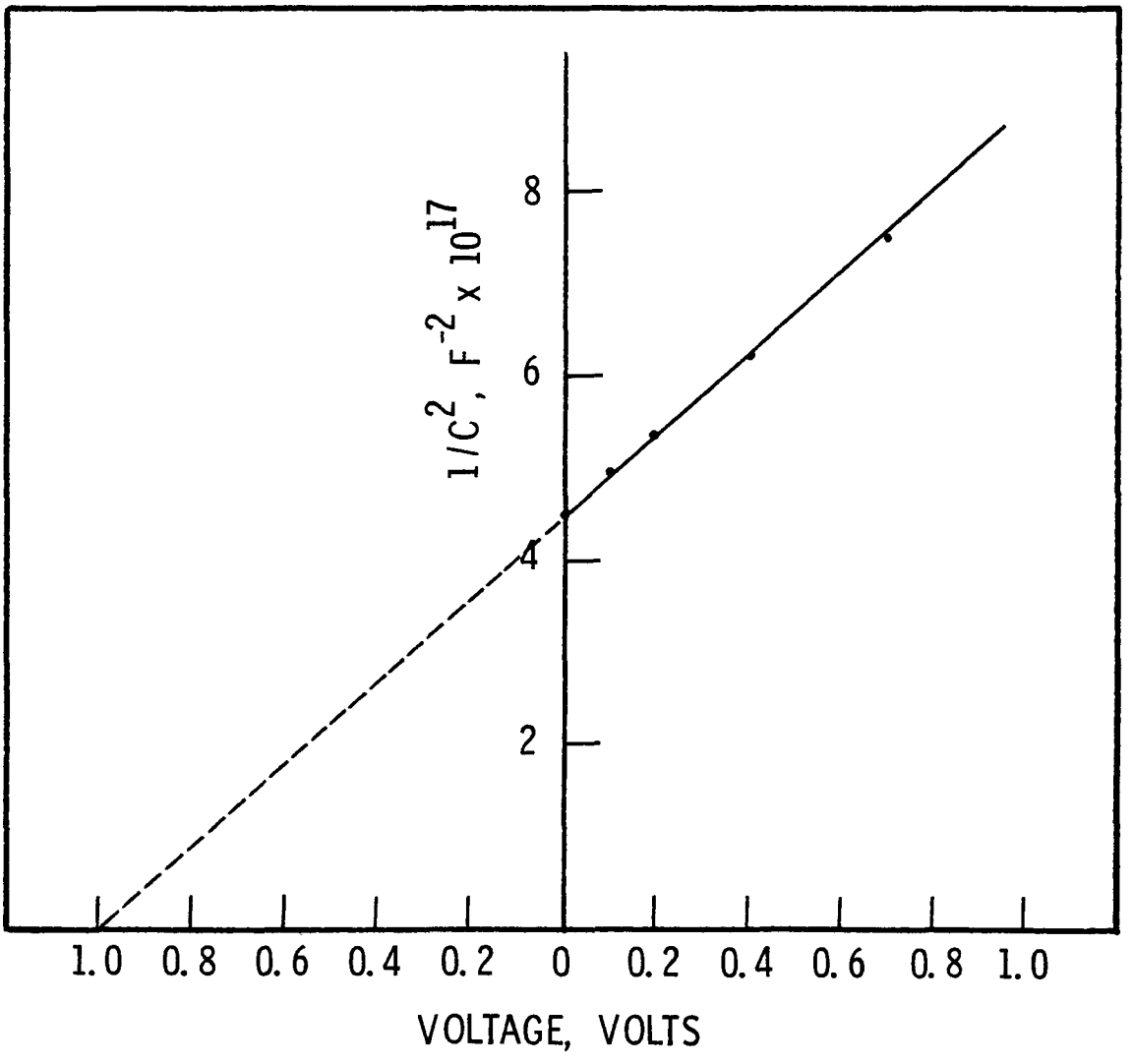


Figure 21 Capacitance voltage characteristics of a Ag/oxide/n-GaAs/ n^+-GaAs/W/graphite structure under reverse bias.

barrier height calculated from the intercept on the voltage axis and the Fermi energy is about 1.02 eV.

The characteristics of thin film gallium arsenide solar cells on graphite substrates are similar to those on tungsten/graphite substrates when the gallium arsenide in the GaAs/graphite interface region is doped to a carrier concentration of $5 \times 10^{18} cm^{-3}$ or higher. The dark and illuminated characteristics of a solar cell of 9 cm^2 area on a graphite substrate are shown in Figures 22 and 23, respectively, as an example. The AM1 efficiency of the solar cell is about 6.1%. In general, the conversion efficiency of solar cells on graphite substrates is somewhat lower than that on tungsten/graphite substrates, and the results are also less reproducible.

The results obtained so far are extremely promising. It is believed that an AM1 efficiency of 10% can be achieved by (1) the optimization of gallium arsenide deposition process to improve the uniformity of crystallite size in deposited films, (2) the optimization of the oxidation of gallium arsenide films, (3) the improvement of the deposition of antireflection coatings, and (4) the use of a gallium arsenide phosphide film or a very shallow p-n junction at the surface of the gallium arsenide film to increase the open-circuit voltage of MOS solar cells.

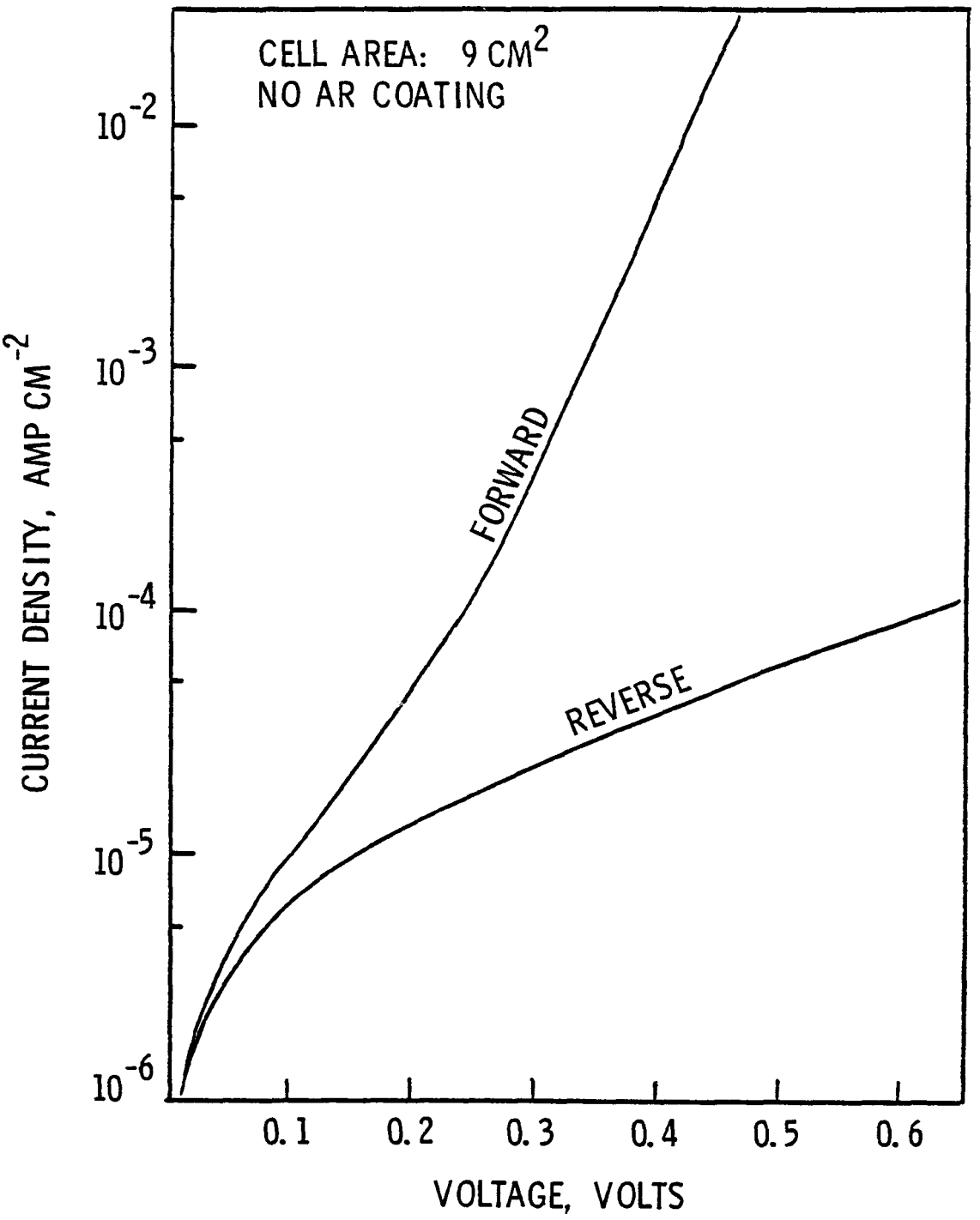


Figure 22 Dark current-voltage characteristics of a Au/oxide/ n-GaAs/n^+-GaAs/graphite solar cell of 9 cm^2 area at room temperature.

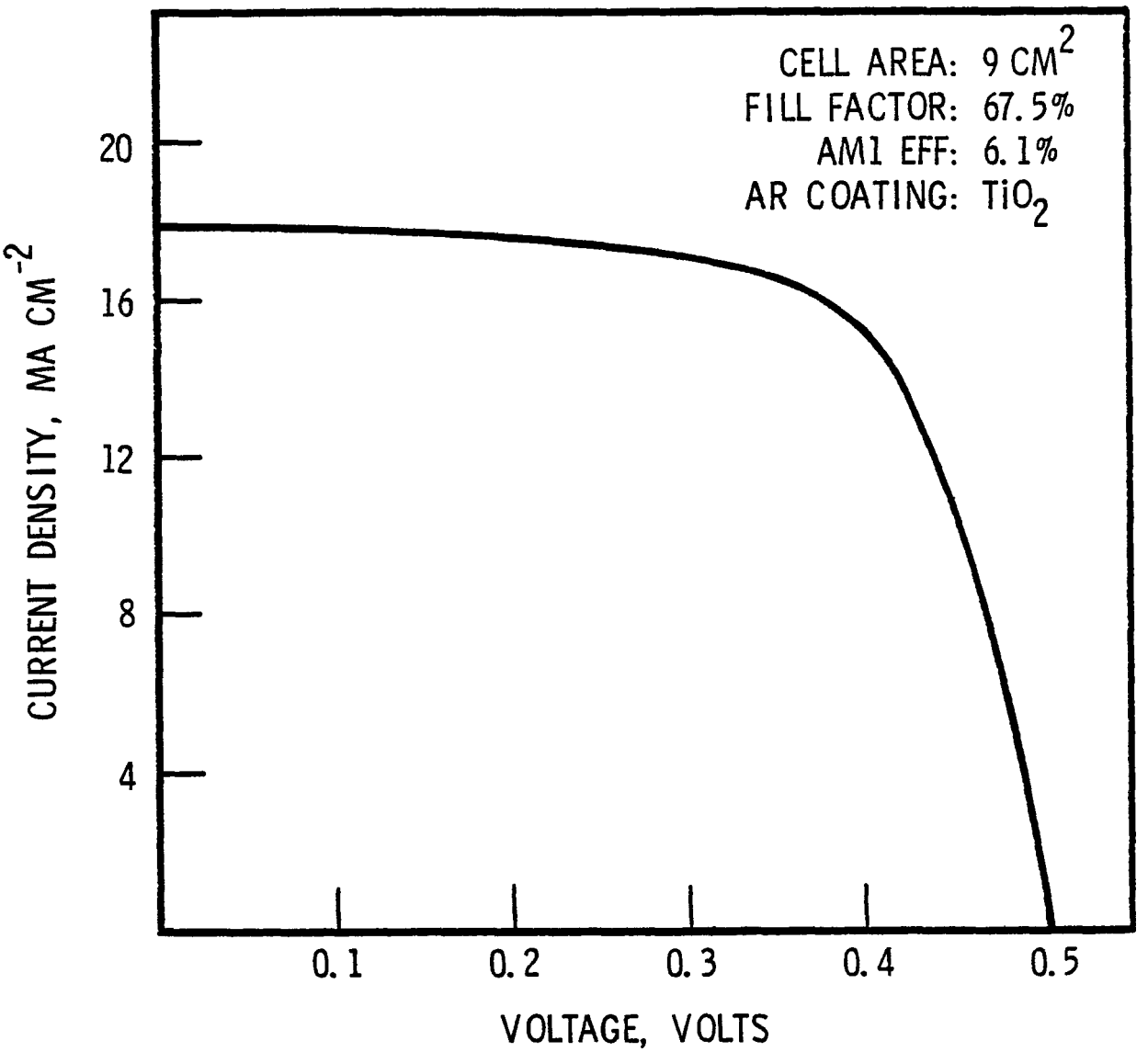


Figure 23 Current-voltage characteristics of a titanium dioxide coated solar cell shown in Figure 22 under illumination with ELH quartz-halogen lamps at AM1 conditions.

V. Stability of Thin Film Gallium Arsenide Solar Cells

To determine the feasibility of using thin film gallium arsenide MOS solar cells for terrestrial applications, some preliminary investigations on the temperature coefficients of solar cell parameters and the stabilities of solar cells under temperature and optical stress have been carried out. The solar cells under study were fabricated from gallium arsenide films on tungsten/graphite substrates in accordance with the techniques discussed in Section IV.2. They are 9 cm^2 in area with an AM1 efficiency in the range of 6 to 6.5% at room temperature. Conducting epoxy was used to attach lead wires to the grid contact and graphite, and an iron-constantan thermocouple was attached to the cell for temperature measurements. The use of silver epoxy for lead attachment is not entirely satisfactory and is used only for preliminary studies; other lead attachment techniques must be developed. The cell was then encapsulated in GE RTV 615 transparent silicone potting compound, and SS-4120 primer was used to insure a strong bond between the cell and the silicone. The results are summarized below.

V.1 Temperature Coefficients of Solar Cell Parameters

The characteristics of a number of thin film gallium arsenide solar cells, including open-circuit voltage, short-circuit current, fill factor, and conversion efficiency have been measured in the temperature range of -30°C to 80°C under illumination with GE ELH quartz-halogen lamps calibrated with a standard silicon cell under AM1 conditions. Cells with both silver and gold as the barrier metal were used, and their dark current-voltage characteristics were also measured. The measurements were carried

out in the order of increasing temperature; both the dark and illuminated characteristics remained unchanged after the high temperature measurements. The data on one cell with silver barrier and one cell with gold barrier are discussed here as examples.

The dark current-voltage characteristics of a gold barrier cell and a silver barrier cell in the temperature range of -30°C to 80°C are shown in Figures 24 and 25, respectively. Both the forward and reverse currents increased with increasing temperature, as expected, and the "n" value in the diode equation remained essentially unchanged. The solar cell characteristics of a gold barrier cell and a silver barrier cell under illumination equivalent to AM1 conditions at different temperatures are shown in Figures 26 and 27, respectively. Both the open-circuit voltage and the AM1 efficiency decreased with increasing temperature, and the short-circuit current density increased with increasing temperature. The open-circuit voltage decreased at a rate of 2.4 mV/°C and 3.2 mV/°C for the gold barrier cell and the silver barrier cell, respectively. The AM1 efficiency decreased at a rate of about 0.03%/°C for silver barrier cells and 0.02%/°C for gold barrier cells. As a comparison, the temperature coefficient of the open-circuit voltage of single crystalline $Ga_{1-x}Al_xAs$-GaAs p-p-n heterojunction solar cells is about -2 mV/°C in the temperature range of -173° to 350°C, and the efficiency decreased at a rate of 0.022%/°C in the temperature range of 25° to 200°C.[12]

V.2 Thermal Stress

To determine the thermal stability of thin film gallium arsenide solar cells, the current-voltage characteristics of the encapsulated cells

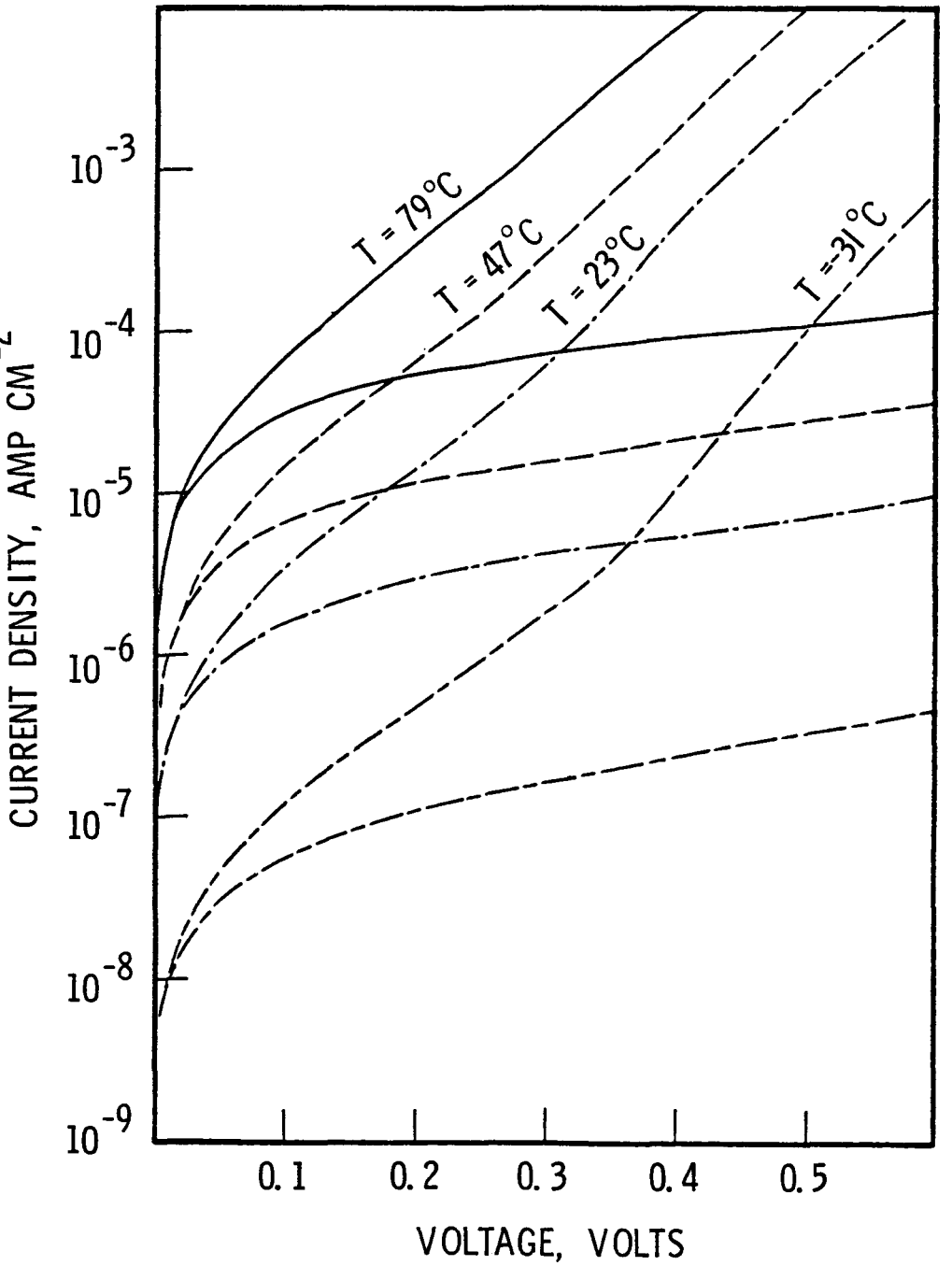


Figure 24 Dark current-voltage characteristics of a TiO_2/Au/oxide/n-GaAs/n^+-GaAs/W/graphite solar cell of 9 cm^2 area at different temperatures.

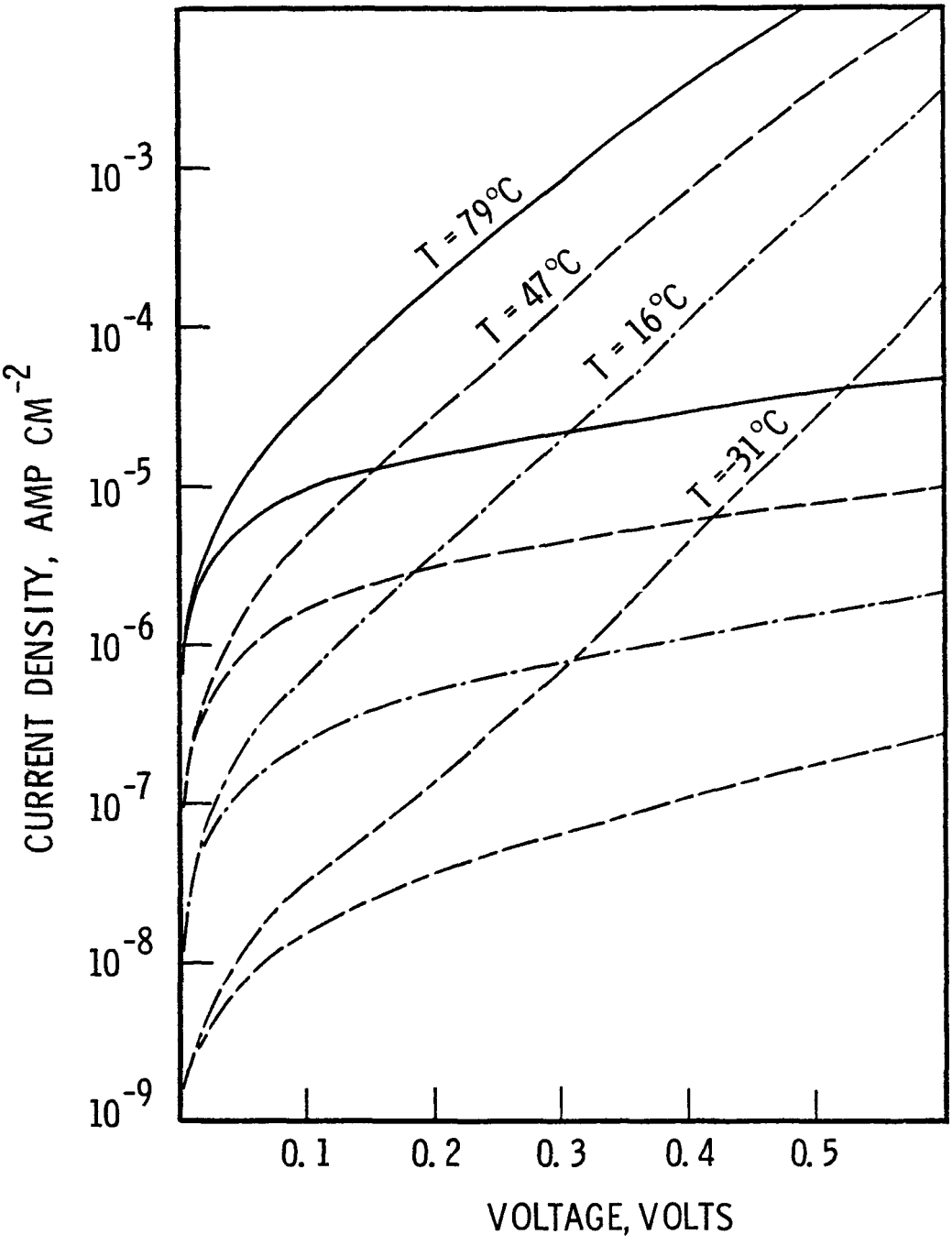


Figure 25 Dark current-voltage characteristics of a TiO_2/Ag/oxide/n-GaAs/n^+-GaAs/W/graphite solar cell of 9 cm^2 area at different temperatures.

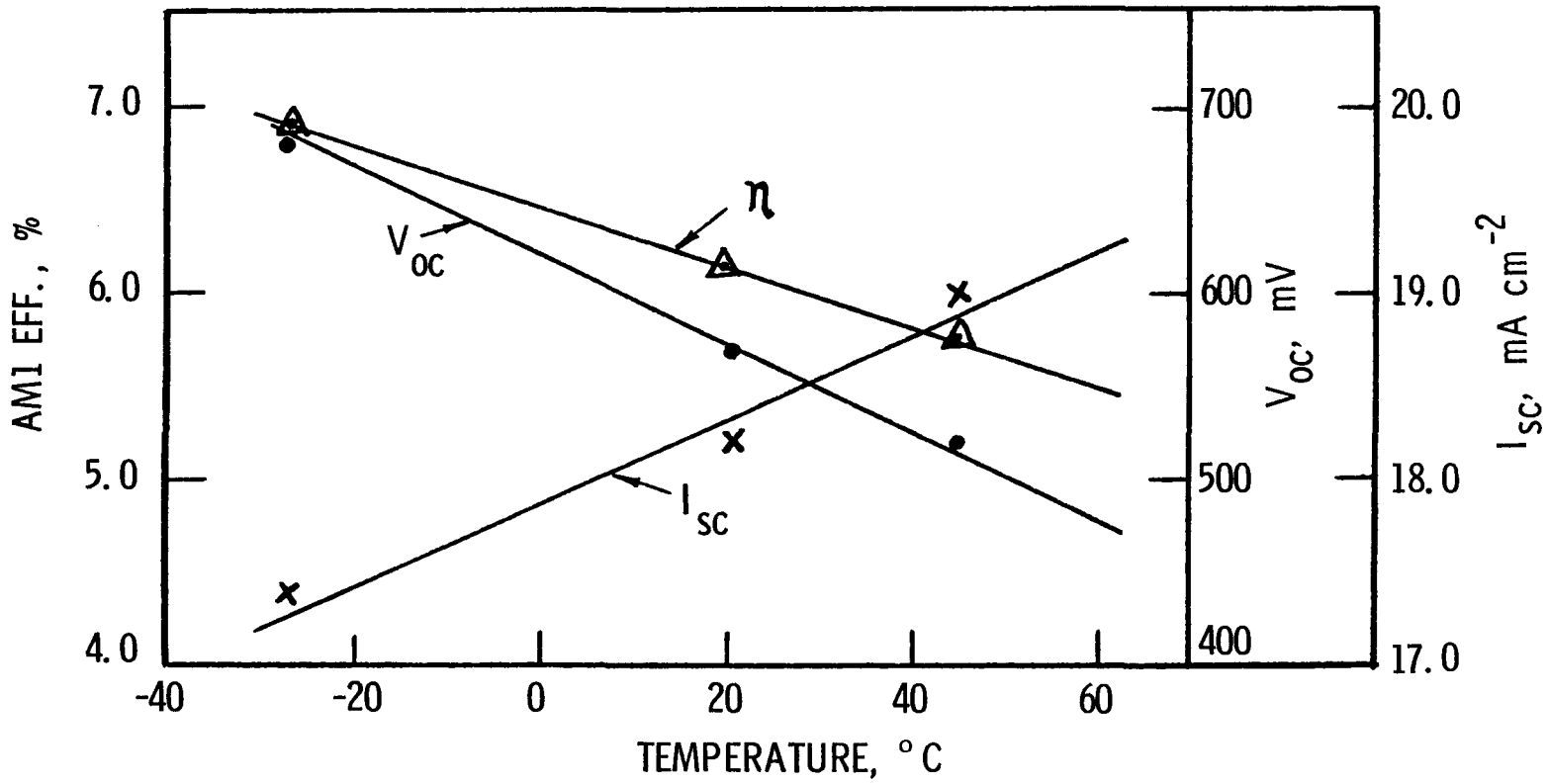


Figure 26 Current-voltage characteristics of a TiO_2/Au/oxide/n-GaAs/n^+-GaAs/W/graphite solar cell as a function of temperatures under illumination with ELH quartz-halogen lamps at AM1 conditions.

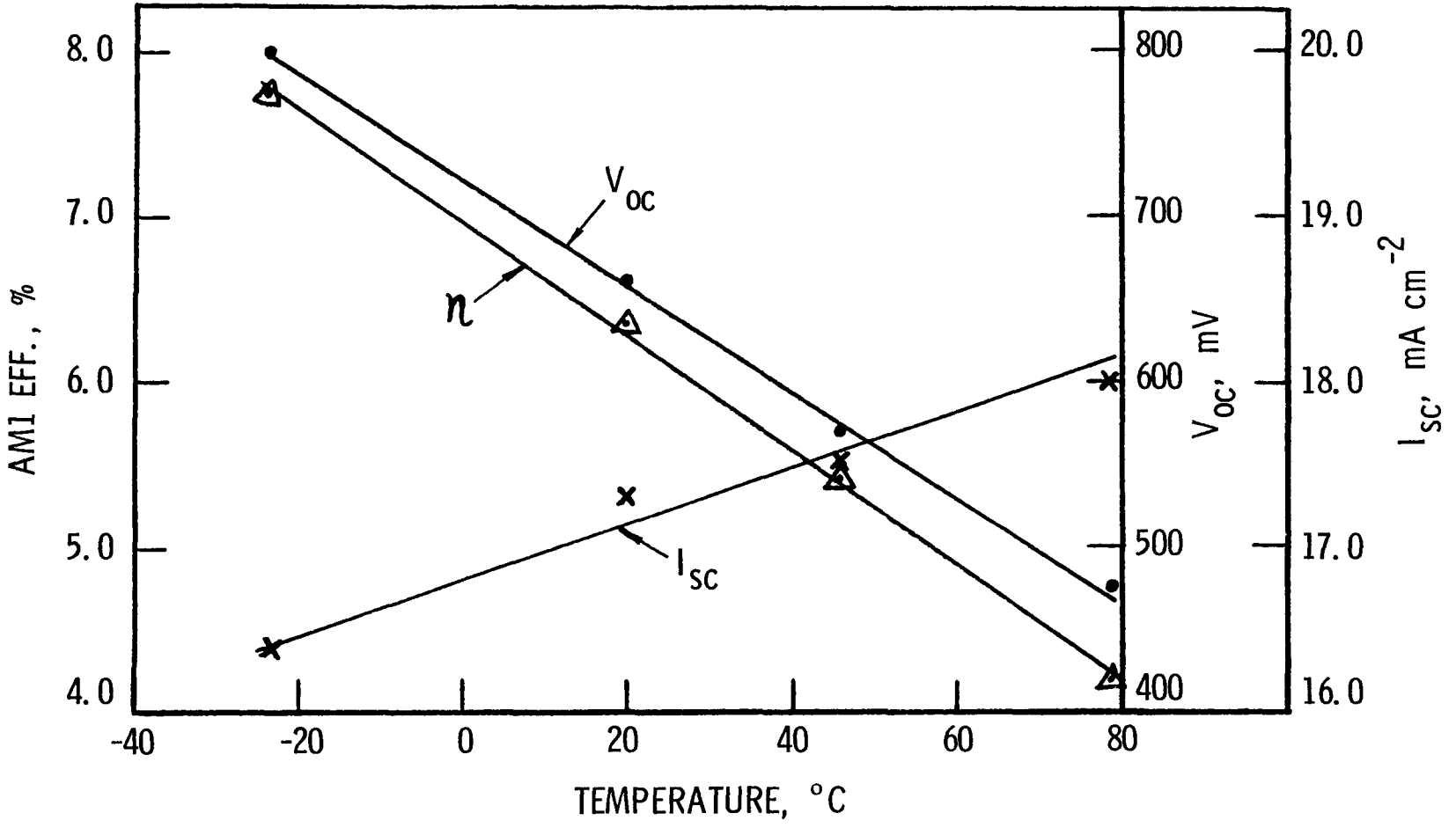


Figure 27 Current-voltage characteristics of a TiO_2/Ag/oxide/n-GaAs/n^+-GaAs/W/graphite solar cell as a function of temperatures under illumination with ELH quartz-halogen lamps at AM1 conditions.

were first measured in the dark and under illumination at room temperature. They were then immersed in a constant temperature bath at 60°C for 24 hours, and their current-voltage characteristics remeasured. The characteristics of gold barrier cells were found to be unchanged. In the case of silver barrier cells, the open-circuit voltage and short-circuit current of the cells remained essentially the same; however, the fill factor degraded by about 9%, due to increased series resistance (Figure 28). It is likely that this increase in series resistance is associated with the increase in the contact resistance of the lead wire.

V.3 Optical Stress

The optical stress test was carried out by placing a gold barrier cell under high illumination conditions (approximately 325 mW/cm^2) with a 0.6 ohm load resistor. The cell was maintained at 50-55°C during the test by forced air cooling. The current through the load and the voltage across the solar cell were 378 mA and 316 mV, respectively, corresponding to a power output of 119 mW. This current and voltage remained relatively constant during a period of more than 48 hours. However, the AM1 efficiency of the solar cell at room temperature degraded by about 9% when measured shortly after the optical stress. The open-circuit voltage, short-circuit current density, fill factor, and AM1 efficiency were 530 mV, 19.6 mA, 60.0%, and 6.25%, respectively, before optical stress. The corresponding properties after optical stress were 510 mV, 19.3 mA, 57.6%, and 5.68%, respectively (Figure 29). Nevertheless, the characteristics of the solar cell recovered after standing at room temperature for about 4-5 hours.

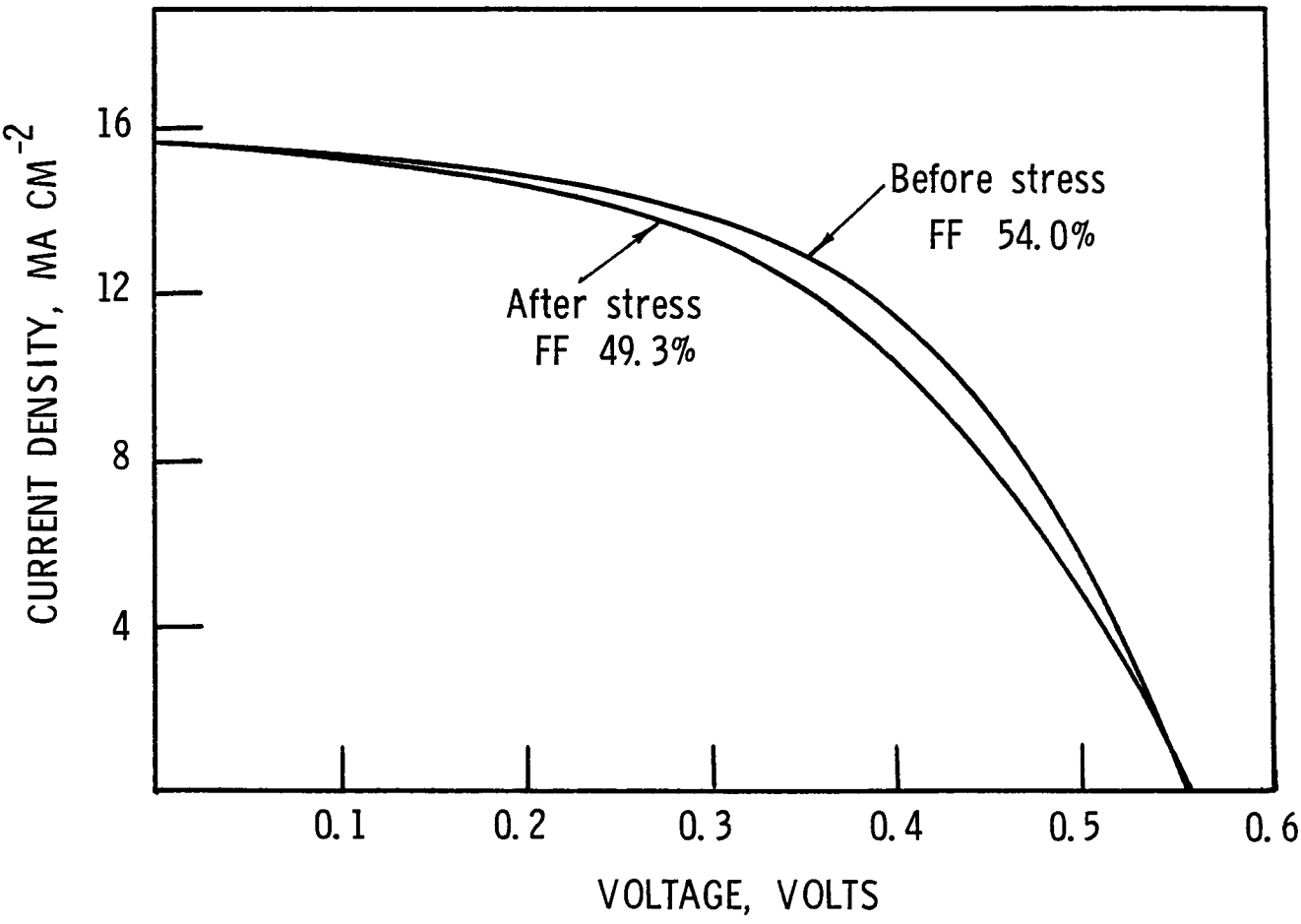


Figure 28 Current-voltage characteristics of a TiO_2/Ag/oxide/n-GaAs/n^+-GaAs/W/graphite solar cell under illumination at AM1 conditions before and after thermal stress.

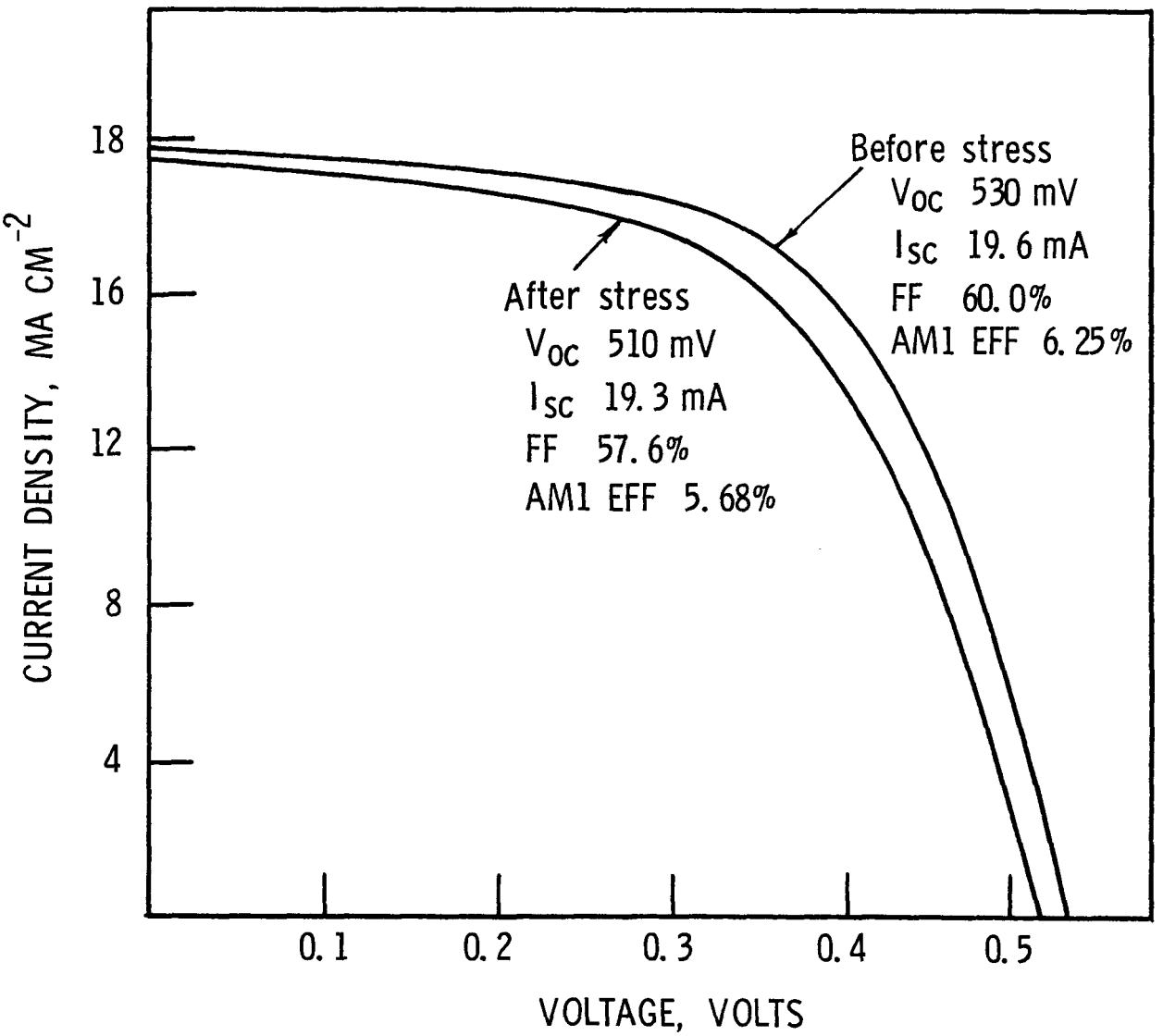


Figure 29 Current-voltage characteristics of a TiO_2/Au/oxide/n-GaAs/n^+-GaAs/W/graphite solar cell under illumination at AM1 conditions before and after optical stress.

VI. References

(1) Shirley S. Chu, "Thin Films of Gallium Arsenide on Low Cost Substrates," Annual Report, ERDA Contract E(04-3)-1284, September, 1977.

(2) S. W. Ing and H. T. Minden, "Open Tube Epitaxial Synthesis of GaAs and GaP," J. Electrochem. Soc., 109, 995 (1962).

(3) J. R. Knight, D. Effer, and P. R. Evans, "The Preparation of High Purity Gallium Arsenide by Vapor Phase Epitaxial Growth," Solid State Electronics, 8, 178 (1965).

(4) J. J. Tietzen and J. A. Amick, "The Preparation and Properties of Vapor-Deposited Epitaxial $GaAs_{1-x}P_x$ using Arsine and Phosphine," J. Electrochem. Soc., 113, 724 (1966).

(5) M. Rubenstein and E. Myers, "Epitaxial Synthesis of GaAs Using a Flow System," J. Electrochem. Soc., 113, 365 (1966).

(6) G. Giesecke and H. Pfister, "Determination of Precision Cell Dimensions of $A^{III}B^{V}$ Compounds," Acta Cryst., 11, 369 (1958).

(7) D. L. Reynard and A. Andrew, "Improvement of Silicon Solar Cell Performance Through the Use of Thin Film Coatings," Applied Optics, 5, 23 (1966).

(8) J. H. Apel, "Optical Coatings for Collection and Conservation of Solar Energy," J. Vac. Sci. Technology, 12, 1016 (1975).

(9) H. J. Hovel, "Transparency of Thin Metal Films on Semiconductor Substrates," J. Appl. Phys., 47, 4968 (1976).

(10) H. J. Hovel, "TiO_2 Antireflection Coatings by a Low Temperature Spray Process," J. Electrochem. Soc., 125, 983 (1978).

(11) H. J. Hovel, "Diffusion Length Measurements by a Simple Photoresponse Technique," in Conf. Record, 12th IEEE Photovoltaic Specialists Conf., Nov. 1976, p. 913.

(12) H. J. Hovel and J. M. Woodall, "$Ga_{1-x}Al_xAs$-GaAs P-P-N Heterojunction Solar Cells," J. Electrochem. Soc., 120, 1246 (1973).

VII. Conclusions

1. The initial stage of deposition of gallium arsenide on tungsten/graphite substrates by the reaction of gallium, hydrogen chloride, and phosphine consists of a high density of small crystallites, and continuous films can be obtained after about 1 minute of deposition.
2. The addition of hydrogen chloride to the reactant mixture has been found to increase considerably the average crystallite size in gallium arsenide films deposited on tungsten/graphite substrates.
3. The reaction between gallium arsenide, hydrogen chloride, and arsenic is also a promising technique for the deposition of solar cell quality gallium arsenide films on tungsten/graphite substrates.
4. The initial stage of deposition of gallium arsenide on graphite substrates consists of many islands of relatively large crystallites, in contrast to that on tungsten/graphite substrates.
5. The n-GaAs/graphite interface is rectifying. However, the interface resistance can be reduced sufficiently for solar cell purposes by using an n^+-GaAs layer at the interface.
6. Titanium dioxide films have been deposited as antireflection coatings for solar cells at 80-100°C by the hydrolysis of tetraisopropyl titanate in a conventional chemical vapor deposition system.
7. Thin film MOS solar cells of 9 cm^2 area have been prepared from gallium arsenide deposited on graphite and tungsten/graphite substrates. The AM1 efficiencies are about 6.5% for solar cells on tungsten/graphite substrates and are about 6% for solar cells on graphite substrates. The objectives of this phase of the program has been fulfilled.

8. The temperature coefficients of open-circuit voltage and conversion efficiency of gold barrier thin film gallium arsenide solar cells are similar to those of single crystalline gallium arsenide heterojunction cells, the silver barrier cells have higher temperature coefficients.
9. The gold barrier cells are more stable than silver barrier cells after prolonged heat treatment at 60°C.
10. Gold barrier cells operated under high illumination levels at 50-55°C have shown good stability.

VIII. Plan for the Next Period

1. Deposition of gallium arsenide films on tungsten/graphite and graphite substrates with emphasis on the effects of crystallite size, porosity, and roughness on the solar cell characteristics.
2. Determination of n-GaAs/substrate interface resistance as a function of dopant concentration in the interface region.
3. Investigation of the effects of oxidation techniques (i.e., dry oxygen at elevated temperatures or wet oxygen at room temperature) on the composition of oxidation product and the characteristics and stability of solar cells.
4. Investigation of the use of thin films of $GaAs_xP_{1-x}$ ($x > 80\%$) for the fabrication of MOS solar cells.
5. Investigation of the use of a shallow p-n junction at the surface of gallium arsenide films for the fabrication of MOS solar cells.
6. Continuation of the studies of the stability of thin film gallium arsenide solar cells.

IX. Publications

IX.1 Oral Presentations

1. "Thin Film Gallium Arsenide Solar Cells," presented at the 152nd National Meeting of the Electrochemical Society, Atlanta, Georgia, October, 1977. Extended Abstracts, 77-2, 1116 (1977).

2. "Stability of Thin Film Gallium Arsenide Solar Cells," presented at the Stability of Solar Cells and Materials Workshop, Gaithersburg, Maryland, May 1-3, 1978.

3. "Large Area Thin Film Gallium Arsenide Solar Cells," 13th IEEE Photovoltaic Specialists Conference, Washington, D. C., June 5-8, 1978.

4. "Thin Film Gallium Arsenide Solar Cells," presented at the Subpanel Meeting on Thin Film Solar Cells, American Physical Society Study on Solar Energy Conversion, June 9, 1978, Washington, D. C.

5. "Thin Film Gallium Arsenide Solar Cells," presented at the MIT Lincoln Laboratory Solid State Seminar, Lexington, Massachusetts, September 12, 1978.

6. "Large Area Thin Film Gallium Arsenide Solar Cells, presented at the 154th National Electrochemical Society Meeting, Pittsburgh, Pennsylvania, October 16-20, 1978.

IX.2 Scientific Papers

1. "Germanium Films on Graphite Substrates," Thin Solid Films, 46, L1 (1977).

2. "Gallium Arsenide Films on Recrystallized Germanium Films," J. Appl. Phys., 48, 4848 (1977).

3. "Thin Film Gallium Arsenide Solar Cells on Tungsten/Graphite Substrates," Appl. Phys. Letters, 32, 557 (1978).

4. "Gallium Arsenide Films on Tungsten/Graphite Substrates," J. Electrochem. Soc., 125, 1668 (1978).

5. "Gallium Arsenide Films and Solar Cells on Graphite Substrates," J. Appl. Phys., submitted for publication.