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THIN FILMS OF GALLIUM ARSENIDE ON LOW-COST SUBSTRATES

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Summary

This is the First Annual Project Report on "Thin Films of Gallium Arsenide on Low Cost Substrates" sponsored by the U. S. Energy Research and Development Administration under Contract No. E(04-3)-1284. The objective of this program is to conduct intensive studies concerning thin films of gallium arsenide on low cost substrates as an initial step for the fabrication of low cost thin film solar cells of relatively high efficiency and long life.

Efforts during this year have been directed to (1) the construction of two gallium arsenide deposition systems using the halide process, (2) the preparation of tungsten/graphite and germanium(recrystallized)/tungsten/graphite substrates, (3) the deposition and characterization of gallium arsenide on tungsten/graphite substrates, and the fabrication and characterization of thin film gallium arsenide solar cells, and (4) the deposition and characterization of gallium arsenide films on germanium(recrystallized)/tungsten/graphite substrates and the fabrication of solar cells.

Gallium arsenide films have been deposited on W/graphite substrates under a wide range of substrate temperature and reactant composition, and their properties have been evaluated. Films deposited under optimum conditions have an average crystallite size of about 15 μm and are essentially polycrystalline. Schottky barriers on these films do not exhibit ideal behaviors. MOS type solar cells with an AM1 efficiency (no AR coatings) of up to 3.5% have been produced.

Gallium arsenide films deposited on Ge(recrystallized)/W/graphite substrates have considerably larger crystallites with a strong {111} preferred orientation and contains a high concentration of germanium, about 10^{17} cm^{-3}. Solar cells from these films have poor characteristics due to the high diffusion rate of germanium along grain boundaries.

I. Introduction

This is the First Annual Project Report of a research program "Thin Films of Gallium Arsenide on Low Cost Substrates" supported by the Division of Solar Energy of the U. S. Energy Research and Development Administration under Contract No. E(04-3)-1284. The objective of this contract is to perform intensive studies concerning thin films of gallium arsenide on low cost substrates as an initial step in a program aimed at the design and fabrication of arrays of extremely low-cost thin-film photovoltaic cells of relatively high efficiency and long life.

Although single crystalline silicon solar cells are the best known photovoltaic energy converter at present, gallium arsenide solar cells have been under study since the fifties. Gallium arsenide solar cells have a higher theoretical conversion efficiency than silicon solar cells(1) and can also operate at higher temperatures because of the larger energy gap of gallium arsenide, 1.43 eV, at room temperature. In addition, gallium arsenide being a direct-gap semiconductor has a very sharp absorption edge, and solar radiation with energy in excess of the energy gap is essentially all absorbed within a few micrometers of the surface compared to about one hundred micrometers for silicon. Since the photovoltaic effects in gallium arsenide were first reported in 1954,(2) continued improvements in the conversion efficiencies of single crystalline gallium arsenide solar cells have been achieved. Under terrestrial sunlight, the conversion efficiency of gallium arsenide solar cells with a gallium-aluminum arsenide window is up to 21%,(3) and that of MIS type gallium arsenide solar cells is about 15%.(4)

Single crystalline gallium arsenide solar cells are very expensive at present. However, the high optical absorption constants of gallium arsenide suggest that the use of thin film gallium arsenide solar cells is a promising approach for the fabrication of low cost high efficiency solar photovoltaic conversion systems. Recent calculations have shown that the AM 1 efficiency of thin film gallium arsenide Schottky barrier solar cells can approach 12% for gallium arsenide crystallite sizes of 3 μm or greater.(5) Thus, the use of a thin film of gallium arsenide on a low cost substrate will reduce the material and fabrication costs of gallium arsenide solar cells by a factor of one hundred or more. Very little information is available in the literature regarding gallium arsenide thin film solar cells.

The first thin film gallium arsenide solar cell was reported in 1967.(6) Gallium arsenide films were deposited by sputtering, flash evaporation, and chemical transport techniques; the transported films had the best optical absorption characteristics, and the conductivity type and resistivity of sputtered and flash evaporated films were difficult to control. Gallium arsenide films deposited on molybdenum and aluminum substrates by the chemical transport technique with steam as the transport agent were used for the fabrication of three types of solar cells: p-n homojunctions, p-n heterojunctions, and surface barriers. P-n homojunctions formed by zinc diffusion were unsatisfactory because of the rapid diffusion of zinc along grain boundaries. The p-n junctions formed by chemical transport were also unsuitable because of the high sheet resistance of the p-layer. Heterojunctions formed by depositing gallium phosphide films onto gallium arsenide films had poor electrical characteristics. Schottky barrier solar cells using evaporated platinum as the barrier metal on gallium arsenide films deposited on molybdenum substrates had more satisfactory characteristics. The barrier height, measured from the dark I-V characteristics, was approximately 0.75 eV. The spectral response of Pt/GaAs cells were not notably different from that of gallium arsenide p-n junction cells. Under illumination at 100 mW/cm^2, the conversion efficiencies were 3%, 4.5%, and 5% for cells of 4 cm^2, 2 cm^2, and 0.2 cm^2 area, respectively. Recently, gallium arsenide films have been deposited on tantalum and molybdenum substrates by the reaction of trimethylgallium and arsine with the objective of fabricating solar cells.(7,8) However, the conversion efficiencies of Schottky barrier cells on tantalum substrates were considerably lower than those reported earlier.(8)

The technical 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. The substrates were selected on the basis of their structural, chemical, electrical, and mechanical properties. Graphite is an attractive substrate for the deposition of gallium arsenide films because of its relatively low cost, chemical inertness, high electrical conductivity, and the availability of several types of graphite with a thermal expansion coefficient similar to that of gallium arsenide. However, the gallium arsenide/graphite interface was found to have a high electrical resistance, and a tungsten interlayer was used to minimize this interfacial resistance. Gallium arsenide films deposited on tungsten/graphite substrates cannot be expected to have large crystallites, 1 mm for example, because of the polycrystalline nature of tungsten. When it is desirable to have large crystallites in gallium arsenide films to reduce the loss of light-generated carriers at grain boundaries, the structural properties of the substrate are particularly important. Germanium has the same crystal symmetry as gallium arsenide, and the lattice parameter and thermal expansion coefficient of germanium (5.657 Å, 5.9 x 10^{-6} °C^{-1}) are very similar to those of gallium arsenide (5.654 Å, 6.8 x 10^{-6} °C^{-1}). Thus, germanium is a suitable substrate for the deposition of polycrystalline gallium arsenide films. Although germanium is not a low cost substrate, polycrystalline germanium films can be readily deposited on a low cost support by the thermal reduction of germanium tetrachloride and can be recrystallized to yield large crystallites. Therefore, a recrystallized germanium film on a tungsten/graphite support has been selected as a substrate for the deposition of gallium arsenide films (the use of a tungsten interlayer is essential since molten germanium does not wet graphite).

During the first year of this program, major efforts were directed to (1) the construction of gallium arsenide deposition systems, (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 summarized in the following sections.

II. Chemical Vapor Deposition of Gallium Arsenide

II.1. Technical Discussion

The chemical vapor deposition technique in a gas flow system has been used extensively for the deposition of gallium arsenide films. This technique has two distinct advantages: (1) a wide range in thickness from a fraction of a micrometer to hundreds of micrometers can be achieved and controlled, and (2) the dopant concentration and distribution in deposited gallium arsenide can be controlled to an extent not obtainable by other techniques. A number of chemical reactions have been used for the deposition process. It is essential that the chemical reaction is predominately heterogeneous taking place on the substrate surface. In contrast, volume reaction results in the formation of molecular clusters of random orientations in the space surrounding the substrate, and the deposition of these clusters on the substrate will produce non-adherent deposit. Furthermore, the by-products of the reaction must be volatile at the processing temperature to insure high purity of the deposit. The dopant concentration and distribution can be readily controlled by programming the composition of the reactant mixture. Gallium arsenide films have been deposited by the following reactions:

(1) Hydrogen chloride, gallium, and arsenic:(9) 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. Hydrogen chloride is used to convert gallium into gallium monochloride, and 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:

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

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

(2) Arsenic trichloride, hydrogen, and gallium:(10) In this process, a two zone furnace is used to maintain gallium at 800-850°C and the substrate at 750-800°C. Hydrogen is used as a carrier gas to introduce arsenic trichloride to the gallium zone, where the reduction of arsenic trichloride yields arsenic vapor and hydrogen chloride, and hydrogen chloride reacts with gallium to form gallium monochloride. Arsenic and gallium monochloride are carried over the substrate surface to deposit gallium arsenide. The chemical reactions are:

$4\ AsCl_3(g) + 6H_2(g) \rightarrow As_4(g) + 12HCl(g)$

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

$6GaCl(g) + As_4(g) \rightarrow 4GaAs(s) + 2GaCl_3(g)$

(3) Hydrogen chloride, gallium, and arsine:(11) In this process, a two-zone furnace is used to maintain gallium at 800-850°C and the substrates at 750-800°C. Similar to (1) and (2), gallium is converted into gallium monochloride which reacts with arsine on the substrate surface to deposit gallium arsenide. The chemical reactions are:

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

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

(4) Gallium trichloride, hydrogen, and arsenic:(12) In this process, gallium trichloride is reduced by hydrogen in the presence of arsenic on the surface of the substrate at 650-700°C. The chemical reaction may be written as:

$4GaCl_3(g) + As_4(g) + 6H_2(g) \rightleftarrows 4GaAs(s) + 12HCl(g)$

(5) Organogallium compounds and arsine:(13) In this process, the reaction between trimethylgallium and arsine takes place on the substrate surface at about 700°C according to the equation:

$(CH_3)_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3CH_4(g)$

Gallium diethylchloride may be used in place of trimethylgallium.(14)

A number of dopants have been incorporated into gallium arsenide films during the deposition process. Zinc, cadmium, and their compounds (such as diethylzinc)(15), are the most commonly used p-type dopants. Silicon, tin, sulfur, selenium, tellurium, and their compounds (such as hydrogen sulfide and hydrogen selenide)(16), are the most commonly used n-type dopants. The energy levels of many dopants in gallium arsenide are well established.(17) Silicon, germanium, tin, selenium, and tellurium are shallow donors with ionization energies of the order of a few millielectronvolts. The ionization energies of magnesium, cadmium, and zinc are 12, 21, and 24 millielectronvolts, respectively. Iron and copper are deep acceptors with multiple levels.

II.2. Experimental

The reaction between gallium, hydrogen chloride, and arsine has been selected for the deposition of gallium arsenide films in this program because of its simplicity. Since the existing apparatus for the deposition of gallium arsenide does not have sufficient flexibility, two gallium arsenide deposition systems have been constructed during the first quarter of this program as shown schematically in Figure 1. Each system consists of two parts: a gas flow control panel and a reaction tube heated by a

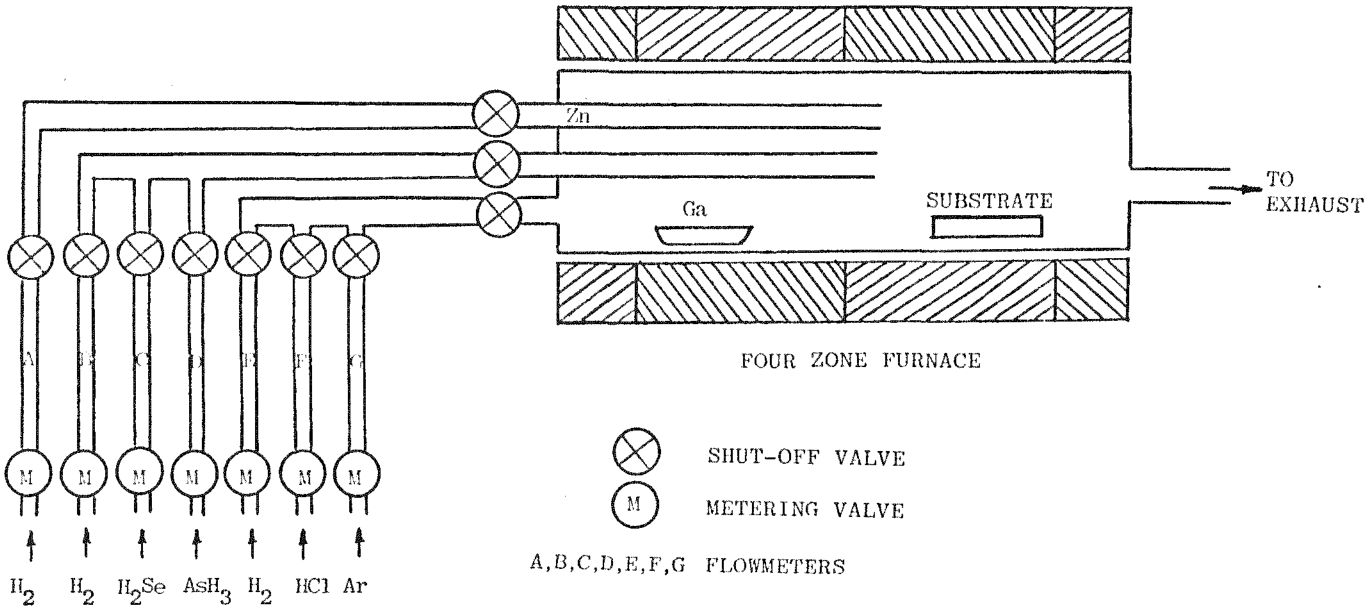

Fig. 1 Schematic diagram of the apparatus for the deposition of gallium arsenide films.

four-zone or a five-zone furnace. On the gas control panel, flowmeters and valves are used to control the flow of the reactants (hydrogen, hydrogen chloride, and arsine) and dopants (hydrogen sulfide as the n-type dopant, and zinc carried by hydrogen as the p-type dopant). The fused silica reaction tube is of 55 mm ID and 59 mm OD; the use of a relatively large diameter reaction tube facilitates the preparation of large area gallium arsenide films of uniform properties. The reaction tube is held in a four-zone or a five-zone resistance-heated furnace with each zone separately heated and controlled; the five-zone furnace allows sufficient flexibility in obtaining the desired temperature profile in the gallium and the substrate zones and also provides the desired control for the temperature of zinc. A temperature profile of the five zone furnace and the positions of gallium, substrate, and zinc in the furnace as shown in Figure 2. Zinc was placed in a fused silica container and was carried to the substrate surface by its vapor pressure or by using hydrogen as a carrier gas. 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, where gallium is converted into volatile gallium monochloride. 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.

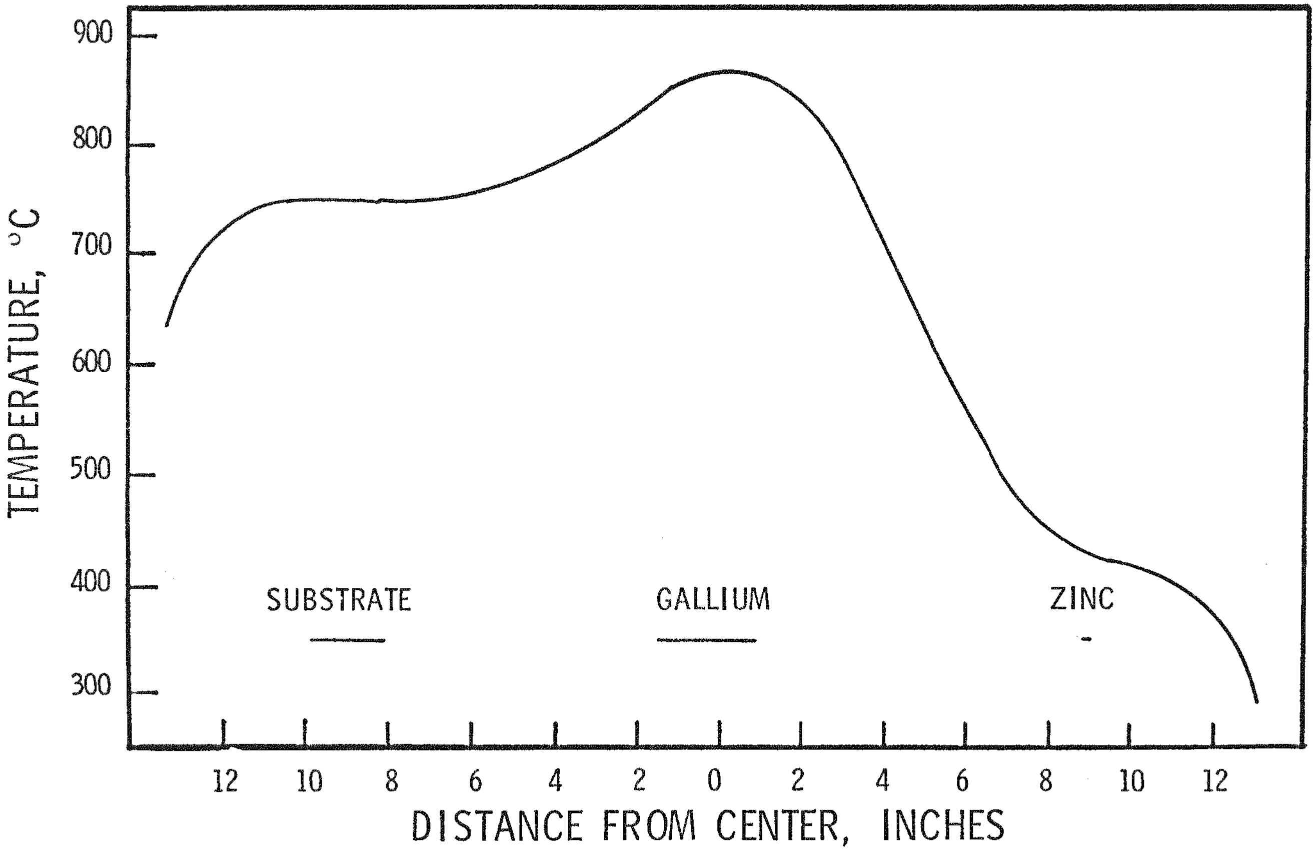

Fig. 2 Temperature profile of a five-zone furnace for the deposition of gallium arsenide films by the reaction of gallium, hydrogen chloride, and arsine in a gas flow system.

II.3. Gallium Arsenide Films on Single Crystalline Gallium Arsenide Substrates

To evaluate the capability of the gallium arsenide deposition systems, a number of deposition experiments were carried out using {100} oriented single crystalline gallium arsenide slices as substrates. The substrates with mechanically lapped surfaces were etched with a 3:1:1 H_2SO_4: H_2O_2: H_2O solution at 80°C for about 2 min. to remove mechanical damage. In some cases, the substrate surface was in-situ etched to assure a clean surface for the deposition process. A hydrogen-hydrogen chloride mixture containing 3-5% hydrogen chloride was used, and for convenience, the substrate temperature used for etching was the same as the deposition temperature. Under these conditions, however, the etching process was preferential, and dislocation pits were revealed after about 2 min. of etching. During the deposition process, the temperatures of gallium and the substrate were in the range of 880-890°C and 720-760°C, respectively. The flow rate of hydrogen was 2ℓ/min, and those of hydrogen chloride and arsine were in the range of 5-15 mℓ/min and 15-45 mℓ/min, respectively (an excess of arsine was used in all experiments to minimize the arsenic deficiency in the deposit). No dopants were added intentionally. The deposition rate of gallium arsenide was about 0.5 μm/min at hydrogen chloride and arsine flow rates of 5 and 15 mℓ/min, respectively, and was about 1 μm/min at hydrogen chloride and arsine flow rates of 15 mℓ/min and 45 mℓ/min, respectively. The thickness of gallium arsenide deposit was determined from the direct measurement of vertically cross-sectioned and etched surfaces.

The as-deposited surface of gallium arsenide films on single crystalline gallium arsenide substrates was similar to the substrate in appearance. They showed no structural features, with the exception of dislocation pits from in-situ etching, when examined with an optical microscope. Chemical etching and optical microscope techniques indicate that the deposited gallium arsenide films are single crystalline and epitaxial with respect to the substrate.

Gallium arsenide films deposited on single crystalline substrates without intentional doping are of n-type conductivity, and those deposited on p-type substrates were used for the measurement of Hall mobility and resistivity at room temperature by the van der Pauw method. Four contacts were made by alloying indium dots to the periphery of specimen surface at 500°C in a hydrogen atmosphere or by using a gallium-indium alloy annealed at 400°C. The resistivity of typical epitaxial film is 8.9 ohm-cm at room temperature, and its Hall mobility is 6470 cm^2/V-sec. Neglecting the difference between the Hall mobility and drift mobility, the net carrier concentration is then approximately 1.1×10^{14}. These properties of epitaxial gallium arsenide films are very similar to those reported in the literature, indicating that the gallium arsenide deposition systems constructed in this program are satisfactory.

II.4. Gallium Arsenide Films on Single Crystalline Germanium Substrates.

Since recrystallized germanium films on tungsten/graphite have been selected as a substrate, the deposition of gallium arsenide on single crystalline germanium substrates was also studied in detail in order to establish the optimum conditions for the deposition of gallium arsenide on recrystallized germanium films. Although gallium arsenide and germanium have the same crystal structure and similar lattice parameters and thermal expansion coefficients, the epitaxial growth of gallium arsenide on germanium substrates is complicated by the fact that germanium forms two arsenides, GeAs (m. p.: 737°C), and $GeAs_2$ (m.p.: 732°C). Germanium monoarsenide crystallizes in the monoclinic system with lattice parameters $a = 22.84$ Å, $b = 3.78$ Å, $c = 9.45$ Å, and $\beta = 43.97°$.(18) Germanium diarsenide crystallizes in the orthorhombic system with lattice parameters $a = 14.76$ Å, $b = 10.16$ Å, and $c = 3.728$ Å.(19) To achieve the epitaxial growth of gallium arsenide on germanium, the formation of germanium arsenides during the initial stage of the deposition must be minimized.

II.4.1. The Deposition Process

Single crystalline germanium slices of p-type and n-type conductivity and {100} and {110} orientations were used as substrates. The substrates with saw-cut surfaces were etched with a CP_4 solution (15 HF, 25 HNO_3, and 15 CH_3COOH with 0.3 Br_2 dissolved) for 3-5 min. to remove the mechanical damage. Since the epitaxial growth of gallium arsenide on germanium is more difficult to achieve than the homoepitaxial growth of gallium arsenide and the cleanliness of the substrate surface is an important factor affecting the structural perfection of gallium arsenide, the germanium substrates were in-situ etched with a hydrogen-hydrogen chloride mixture in all deposition experiments. Using hydrogen and hydrogen chloride at flow rates of 2 ℓ/min. and 100 mℓ/min, respectively, the etch rate of germanium at 720-760°C was 3-4 μm/min. In contrast to the etching of gallium arsenide, this hydrogen-hydrogen chloride mixture is a polishing etch for germanium. A series of experiments were carried out for the deposition of gallium arsenide films on germanium substrates without intentional doping. The flow rate of hydrogen was 2 ℓ/min. and the temperature of gallium was 880-890°C in all experiments. The flow rates of hydrogen chloride and arsine were in the ranges of 5-15 mℓ/min and 15-45 mℓ/min, respectively, similar to those used for the homoepitaxial growth of gallium arsenide. The substrate temperature was in the range of 720-780°C. After deposition, the surface of the specimen was examined with an optical microscope, and the thickness of the deposit was determined by the direct measurement of the vertical cross-sectioned surface. Under the flow rate conditions used here, the temperature of the substrate was found to be the most important factor determining the structural perfection of deposited gallium arsenide. At substrate temperatures of 750°C or higher, the deposition rate of gallium arsenide was negligible, and the substrate surface was not uniformly covered after 30 min. of deposition at hydrogen chloride and arsine flow rates of 15 mℓ/min. and 45 mℓ/min, respectively. The best results were obtained at a substrate temperature of about 740°C, where the surface of the deposit was similar to that of the homoepitaxial gallium arsenide. Chemical etching and optical microscopic studies indicated that the deposit is single crystalline and epitaxial with respect to the substrate. At substrate temperatures of 730°C or lower, the structure perfection of gallium arsenide films degraded. The surface of the deposit was not uniform in appearance; while major portions of the surface are mirror-like, some areas appear to be dull. Scanning electron microscope examinations indicate that the dull areas consist of a mosaic of single crystalline grains.

II.4.2. Properties

Under most conditions of deposition, the deposition rate of gallium arsenide films on {100} oriented germanium substrates is about three times higher than that on {110} oriented substrates. For example, using hydrogen chloride and arsine at flow rates of 15 and 45 mℓ/min, respectively, and a substrate temperature of 740°C, the deposition rates of gallium arsenide on {100} and {110} oriented germanium substrates are about 0.7 and 0.2 μm/min, respectively. Gallium arsenide films deposited on both substrates appear to have similar structural properties.

It is well established that foreign impurities and mechanical damage on the substrate surface and contaminants in the reactant mixture and deposition system are major causes of structural defects in epitaxial films. Thus, great care has been taken in the preparation of heteroepitaxial gallium arsenide films on germanium substrates with regard to the cleanliness of the substrate surface, reactant mixture, and deposition system. No macroscopic defects, such as lineage and polycrystalline inclusions, were observed. However, microscopic defects are frequently observed on the surface of heteroepitaxial films, particularly after etching with a 1:2 HNO_3: H_2O mixture for 2-3 min. The etch figures are usually in the form of pits, grooves, etc. associated with dislocations, stacking faults, etc.

Gallium arsenide films deposited on germanium substrates without intentional doping were all n-type. When the germanium substrate was of p-type conductivity, the resistivity of, and Hall mobility in, the gallium arsenide films were measured at room temperature by the van der Pauw technique. Contacts to the gallium arsenide film were made in the same manner as those to homoepitaxial gallium arsenide films. The average resistivity of gallium arsenide films deposited at 740°C at a rate of 0.7 μm/min is about 0.005 ohm-cm, and the Hall mobility of electrons is about 1700 cm^2/V-sec, corresponding to a net carrier concentration of 7.2×10^{17}. Thus, the net carrier concentration is considerably higher than that in homoepitaxial gallium arsenide, resulting in a marked decrease in Hall mobility. The high carrier concentration is due apparently to the incorporation of germanium into gallium arsenide film. The principal mechanism of the "auto-doping" is presumably chemical transport: the dissolution of germanium substrate by the hydrogen chloride formed during the deposition of gallium arsenide, and the subsequent reduction of resulting germanium chloride at the depositing interface. The chemical reactions are:

$$GaC\ell\ (g) + AsH_3\ (g) \rightarrow GaAs\ (s) + H_2\ (g) + HC\ell\ (g)$$

$$Ge\ (s) + 4\ HC\ell\ (g) \underset{\text{auto doping}}{\overset{\text{dissolution}}{\rightleftharpoons}} GeC\ell_4\ (g) + 2\ H_2\ (g)$$

It is believed that the passivation of the back side of germanium substrate with silicon nitride or silicon dioxide will reduce considerably this auto-doping effect.

III. Selection, Preparation, and Properties of Substrates

III.1. Selection of Substrates

The substrate for the deposition of gallium arsenide films for solar cell purposes must possess certain electrical, chemical, mechanical, and structural properties. The substrate must provide a low resistance electrical contact to the active layer, must not introduce impurities into the active layer over the long term, and must be mechanically compatible with the active layer over a wide range of temperature and humidity. Because of the interaction between the substrate atoms and the deposited gallium arsenide molecules, the microstructure and crystallographic properties of gallium arsenide films are strongly influenced by the crystal symmetry, lattice parameters, and crystallite size in the substrate.

Because of the chemical environment in the deposition of gallium arsenide films by the halide process, the choice of substrates is rather limited. Graphite appears to be an economical substrate for large area solar cells. Several types of graphite have a thermal expansion coefficient similar to that of gallium arsenide. Graphite is chemically inert under the conditions used for the deposition of gallium arsenide. Also, graphite has high thermal and electrical conductivities and may be used as an ohmic contact to the solar cell. However, gallium arsenide films deposited on graphite substrates cannot be expected to have large crystallites, several hundred micrometers for example, because of the polycrystalline nature of graphite.

Since the recombination of carriers at grain boundaries is well known, it is desirable to have the largest possible crystallites in gallium arsenide films to reduce the loss of light-generated carriers. Germanium has the same crystal symmetry as gallium arsenide, and the lattice parameter and thermal expansion coefficient of germanium (5.657 Å, 5.9×10^{-6} °C^{-1}) are very similar to those of gallium arsenide (5.654 Å, 6.8×10^{-6} °C^{-1}). Single crystalline epitaxial films of gallium arsenide have been deposited on germanium substrates,(20-24) and germanium is also used as a substrate for the deposition of gallium arsenide phosphide in the fabrication of LED devices. Thus, germanium is a suitable substrate for the deposition of polycrystalline gallium arsenide films. Although germanium is not a low cost substrate, polycrystalline germanium films can be readily deposited on a low cost support by the thermal reduction of germanium tetrachloride. The chemical vapor deposition of germanium is a well-established technique;(25) germanium films have been deposited on metallic substrates, such as molybdenum and tungsten.(26,27) Furthermore, germanium films on tungsten, molybdenum, sapphire, and other foreign substrates have been recrystallized to yield large crystallites.(28-30) Therefore, a recrystallized germanium film on a low cost support has been selected in this program as a substrate for the deposition of gallium arsenide films.

In addition to recrystallized germanium films, tungsten films on a low cost support has also been selected as a substrate for the deposition of gallium arsenide films. Tungsten crystallizes in the body-centered cubic structure with a lattice parameter of 3.165 Å and thermal expansion coefficient of 4.5×10^{-6} °C^{-1}. Tungsten films can be readily deposited by the thermal reduction of tungsten hexafluoride with hydrogen at 450°C and above.(31) Gallium arsenide films with a high degree of orientation have been deposited on single crystalline tungsten substrates.(20)

III.2. Preparation and Properties of Substrates

Graphite was used as the support for the deposition of germanium and tungsten films. The apparatus for the deposition of germanium and tungsten films on graphite is shown schematically in Figure 3. The flow of various gases, such as hydrogen, argon, and tungsten hexafluoride, was directed by using appropriate valves and measured with flowmeters. Hydrogen was purified by diffusion through a palladium-silver alloy. Germanium tetrachloride was introduced into the reaction tube by bubbling hydrogen at a measured rate through the liquid. A Millipore filter was used to remove any solid particles present in the reactant gas. The reaction tube was made of fused silica and was of 55 mm ID. The graphite substrates grade DFP and TAR graphite supplied by POCO Graphite Incorporated, were supported on a graphite susceptor, and the susceptor was heated externally by an rf generator. Prior to the deposition process, the substrates were first heated in hydrogen at 1100-1200°C to remove the surface contaminations.

III.2.1. Tungsten Films on Graphite

The deposition of tungsten on graphite was carried out by using a hydrogen flow rate of 25 ℓ/min; this relatively high flow rate was used to minimize the gas phase nucleation and the thickness variations of the deposit. The flow rate of tungsten hexafluoride was 30 mℓ/min, and the substrate temperature was in the range of 450-750°C. Tightly adherent layers of tungsten were obtained in all cases at rates of up to 1 μm/min. At substrate temperatures of 750°C or higher, the gas phase nucleation

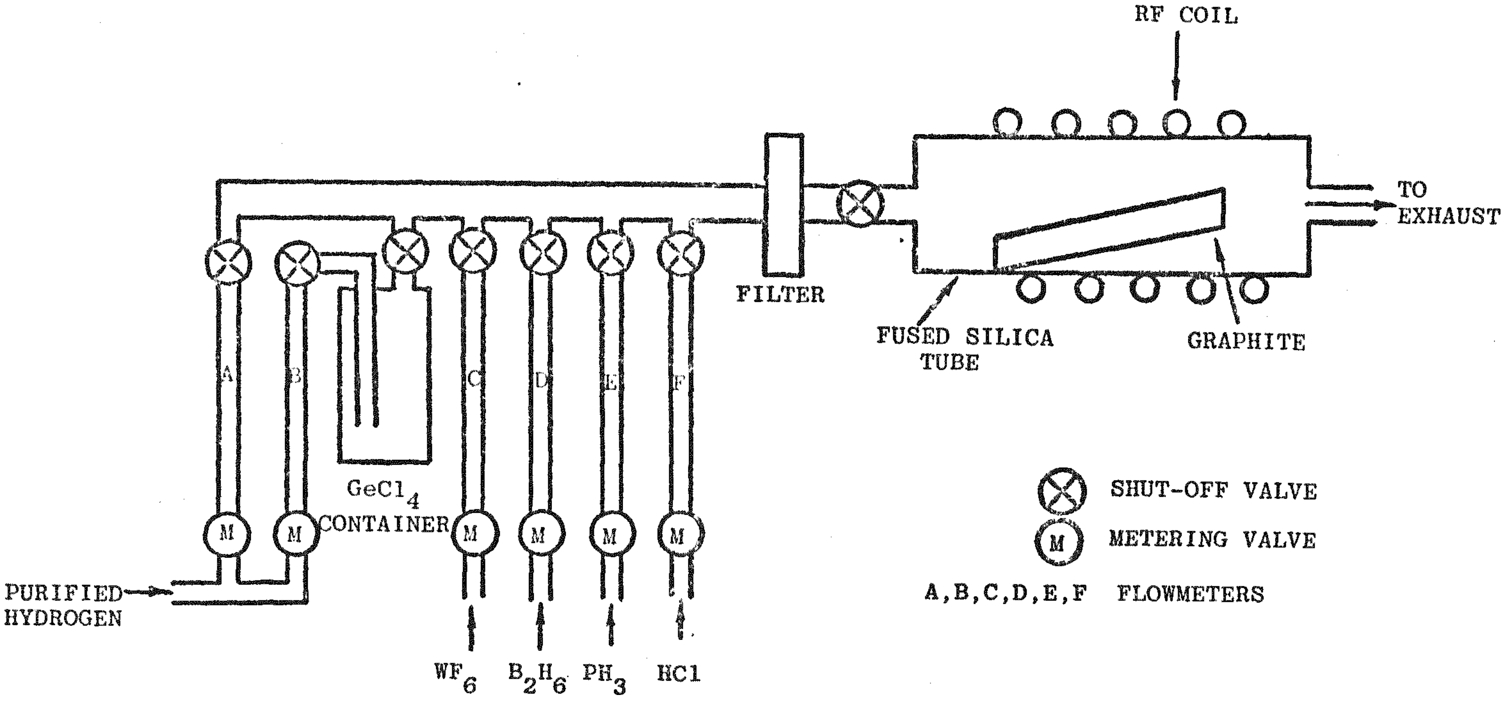

Fig. 3 Schematic diagram of the apparatus for the deposition of germanium and tungsten films on graphite.

became pronounced, and the tungsten deposit contained large crystallites from gas phase reactions. The microstructure and crystallographic properties of tungsten films depend strongly on the deposition temperature, and the size of crystallites increases with increasing temperature. For example, the average size of crystallites in tungsten films of 20-30 μm thickness deposited at 700°C is 10-15 μm, and that in tungsten films of 3-5 μm thickness deposited at 500°C is 1-2 μm. The crystallographic properties of tungsten films deposited on graphite substrates were investigated by the x-ray diffraction technique using General Electric Model XRD-6 diffractometer with CuKα radiation. Polycrystalline tungsten powder of random orientations is known to show three strong diffraction peaks associated with {110}, {200}, and {211} reflections with 2θ values of 40.2°, 58.2°, and 73.2° and relative intensities of 100, 15, and 23, respectively.(32) The diffraction spectra of the tungsten films were obtained by scanning 2θ in the range of 30-80°. The tungsten films deposited at 700°C showed a strong {211} preferred orientation, and those deposited at 500°C showed a strong {100} preferred orientation.

III.2.2. Germanium Films on Graphite

The deposition of germanium was carried out in the temperature range of 750-900°C. A relatively high hydrogen flow rate, about 25 ℓ/min, was used to obtain germanium films of uniform thickness, and the concentration of germanium tetrachloride in the reactant mixture was varied by adjusting the flow rate of hydrogen through the liquid. The substrate temperature and the reactant composition are the most important factors determining the deposition rate and microstructure of germanium films.

At 750° C and below, the deposition rate was negligible. At 850-900°C, no deposition occurred at $GeCl_4/H_2$ molar ratios of less than 2.8×10^{-4}. The rate reached a maximum of about 1 μm/min at a $GeCl_4/H_2$ molar ratio of 2.5×10^{-3} and decreased at higher $GeCl_4/H_2$ molar ratios, essentially negligible at a molar ratio of 5×10^{-3} or higher.

In general, the size of crystallites in germanium films increased with increasing substrate temperature and decreasing deposition rate. For example, the average crystallite size in a germanium film of about 40 μm thickness deposited on graphite at a rate of about 0.4 μm/min is about 20 μm. The crystallographic properties of a number of germanium films were investigated by the X-ray diffraction technique with CuKα radiation. Polycrystalline germanium powder of random orientations is known to show three strong diffraction peaks associated with {111}, {220}, and {311} reflections with 2θ values of 27.3°, 45.3°, and 53.7° and relative intensities of 100, 57, and 39, respectively.(33) The diffraction spectra of the germanium films were obtained by scanning 2θ in the range of 20-60°. Most films exhibited some preferred {111} orientation; the {111}/{220} intensity ratio was usually 3 - 7. The lack of strong preferred orientation in the germanium films is presumably related to the chemical reversibility of the deposition process.

The germanium films deposited on graphite substrates without intentional doping are p-type. To determine the carrier mobility, an n-type germanium film was first deposited on a graphite substrate by using phosphine as a dopant, followed by the deposition of a film without intentional doping. Indium contacts were applied to the as-deposited surface by alloying in a hydrogen atmosphere. The Hall mobility measured by the van der Pauw technique at room temperature is 60-80 $cm^2 v^{-1} sec^{-1}$.

Because of the relatively small size of crystallites in germanium deposited on graphite by the conventional chemical vapor deposition technique, attempts were made to increase the crystallites size by recrystallization. However, molten germanium does not wet graphite, and no uniform films could be obtained after recrystallization.

III.2.3. Germanium (recrystallized)/Tungsten/Graphite Structures

Since molten germanium does not wet graphite, a tungsten interlayer was used to increase the molten germanium-graphite interfacial tension. About 5 μm of tungsten and 15 to 20 μm of germanium were deposited successively on a graphite substrate of 3.5 cm x 15 cm in area. The recrystallization of germanium films on tungsten/graphite substrates was carried out by the unidirectional solidification technique, as shown schematically in Fig. 4. The germanium/tungsten/graphite specimen was placed in a fused silica tube in a hydrogen atmosphere and was heated externally by an rf generator. The temperature profile of the specimen was controlled by adjusting the spacings between the turns of the rf coil to yield a unidirectional temperature gradient of 30-40°C along the length of the specimen. The entire germanium film was first melted, and the power was reduced for the solidification to take place from one end of the specimen to the other. The resulting germanium film has a dendritic structure with elongated grains up to 1 mm long; an example of the recrystallized surface is shown in Fig. 5. X-ray diffraction examinations indicate that the recrystallized germanium films show a strong {111} preferred orientation.

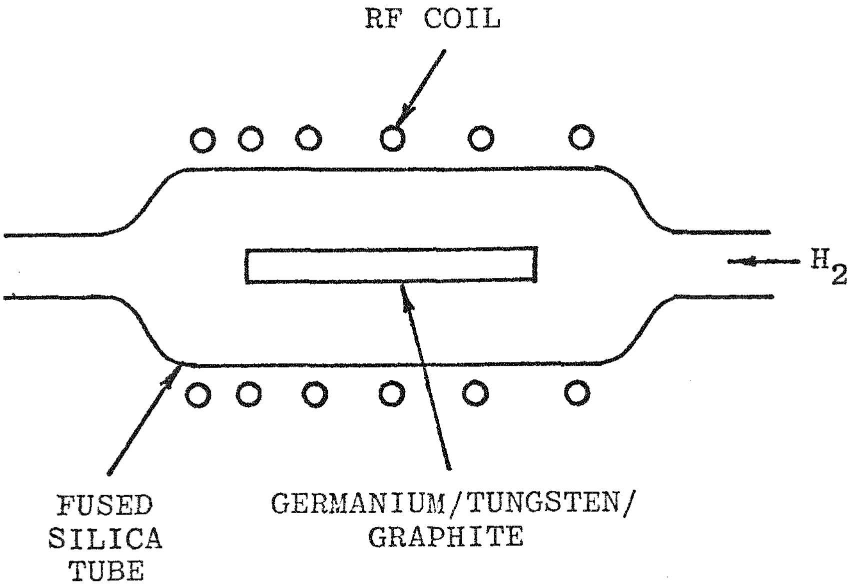

Fig. 4 Schematic diagram of the apparatus for the unidirectional solidification of germanium on tungsten/graphite substrates.

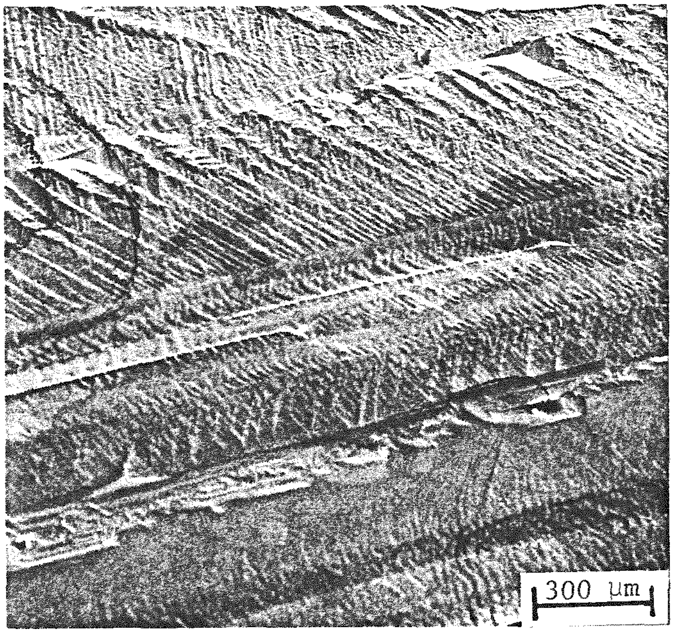

Fig. 5 Scanning electron micrograph of the as-recrystallized surface of germanium on a tungsten/graphite substrate by unidirectional solidification.

The recrystallized germanium film is of n-type conductivity, and its resistivity cannot be measured by the four-point probe technique because of the high conductivity of tungsten/graphite substrates. Spreading resistance measurements indicated that the resistivity of recrystallized germanium films is less than 0.05 ohm-cm. This high conductivity is due to the dissolution of tungsten during the recrystallization process. The recrystallization of p-type germanium films prepared from reaction mixtures with a $B_2H_6/GeCl_4$ molar ratio of up to 10^{-4} also yielded n-type material. P-type germanium films were produced by epitaxial deposition using the thermal reduction of germanium tetrachloride containing diborane on n-germanium (recrystallized)/tungsten/graphite.

IV. Gallium Arsenide Films on Tungsten/Graphite Substrates

Both graphite and tungsten/graphite substrates have been used for the deposition of gallium arsenide films. Qualitatively, the microstructures of the two types of gallium arsenide films are very similar. However, the gallium arsenide/graphite interface has been found to be rectifying, due presumably to the chemical inertness of graphite under conditions used for the deposition of gallium arsenide. Thus, emphasis has been directed to the use of tungsten/graphite substrates during the first phase of this program.

IV.1. Deposition of Gallium Arsenide Films

The tungsten/graphite substrates used for the deposition of gallium arsenide films were of 3.5 cm x 3.5 cm area, and the tungsten film was of about 5 μm thickness deposited at 500°C. The deposition of gallium arsenide films was carried out using the apparatus described in Section II.2. The important process parameters in the deposition of gallium arsenide films are the temperatures of the gallium source and the substrate, and the composition and flow rate of the reactant mixture. A series of experiments were carried out to study the effects of these parameters on the structural and electrical properties of gallium arsenide films on tungsten/graphite substrates. In these experiments, the temperature of gallium, the flow rate of hydrogen, and the flow rate of hydrogen chloride were fixed at 880-890°C, 1 ℓ/min, and 45 mℓ/min, respectively, and the substrate temperature and the $AsH_3/HC\ell$ molar ratio were varied in the range of 725-825°C and 0.5-2, respectively. The use of a relatively high flow rate of hydrogen chloride was found to produce larger crystallites, due presumably to the reduction of rate of nucleation of gallium arsenide.

The thickness of deposited gallium arsenide film was determined by direct measurement on vertical cross-sectioned surfaces in order to determine the average deposition rate. The effect of the reactant composition on the deposition rate of gallium arsenide was pronounced only at the lowest temperature used, 725°C. At 725°C, the average deposition rate was found to increase with increasing $AsH_3/HC\ell$ molar ratio; it increased from 1.2 to 1.5 μm/min as the $AsH_3/HC\ell$ molar ratio was increased from 0.5 to 2. At 750°C and above, the average deposition rate is essentially independent of the $AsH_3/HC\ell$ molar ratio in the range of 0.5-2. These results indicate that the deposition process is surface reaction controlled at 725°C, and that the reaction rate is not rate-limiting at 750°C and higher. At a given reactant composition, the average deposition rate of gallium arsenide peaks at about 750°C, 1.5 μm/min, and decreases with increasing temperature, about 1.2 μm/min at 800°C for example. The lower deposition rate at higher temperatures is presumably related to the thermochemistry of the deposition reaction.

IV.2. Structural Properties of Gallium Arsenide Films

Gallium arsenide films deposited on tungsten/graphite substrates are all polycrystalline, and the as-deposited surfaces were examined with optical and scanning electron microscopes to determine their microstructure. At substrate temperatures of 725° and 750°C, the average crystallite size in gallium arsenide films increases with increasing arsine concentration in the reactant mixture. For example, the average crystallite size in films deposited at 725°C increased from about 5 to more than 10 μm as the $AsH_3/HC\ell$ molar ratio was increased from 0.5 to 2. Figures 6A and 6B show the surface of gallium arsenide films deposited on tungsten/graphite substrates at 725°C using $AsH_3/HC\ell$ molar ratios of 0.5 and 2, respectively, where the effect of $AsH_3/HC\ell$ molar ratio is apparent. At higher substrate temperatures, the $AsH_3/HC\ell$ molar ratio has no appreciable effects on the crystallite size. At a given reactant composition, the substrate temperature has a pronounced effect on the average size of crystallites. At low $AsH_3/HC\ell$ molar ratios, 0.5-1, the average crystallite size increases with increasing substrate temperature, reaching a maximum at 750°-775°C, and then decreases at higher temperatures. Figures 7A and 7B show the surface of gallium arsenide films deposited on tungsten/graphite substrates using a $AsH_3/HC\ell$ molar ratio of 0.5 at 775° and 825°C, respectively. Comparing Figs. 6A, 7A, and 7B, the effect of substrate temperature on the crystallite size in gallium arsenide films deposited at a $AsH_3/HC\ell$ molar ratio of 0.5 is thus apparent. At high $AsH_3/HC\ell$ molar ratios, 2 for example, the average crystallite size is independent of temperature in the range of 725°-775°C and decreases at higher temperatures. The crystallites in all films are of random shape and exhibit no well-developed faces.

The crystallographic properties of gallium arsenide films deposited on tungsten/graphite substrates were examined by the X-ray diffraction technique using CuKα radiation. Polycrystalline gallium arsenide powder of random orientations is known to show three strong diffraction peaks associated with {111}, {220}, and {311} reflections with 2θ values of 27.3°, 45.3°, and 53.8° and relative intensities of 100, 35, and 35.(34) The diffraction spectra of the gallium arsenide films were obtained by scanning 2θ in the range of 20-60°. When the gallium arsenide film was

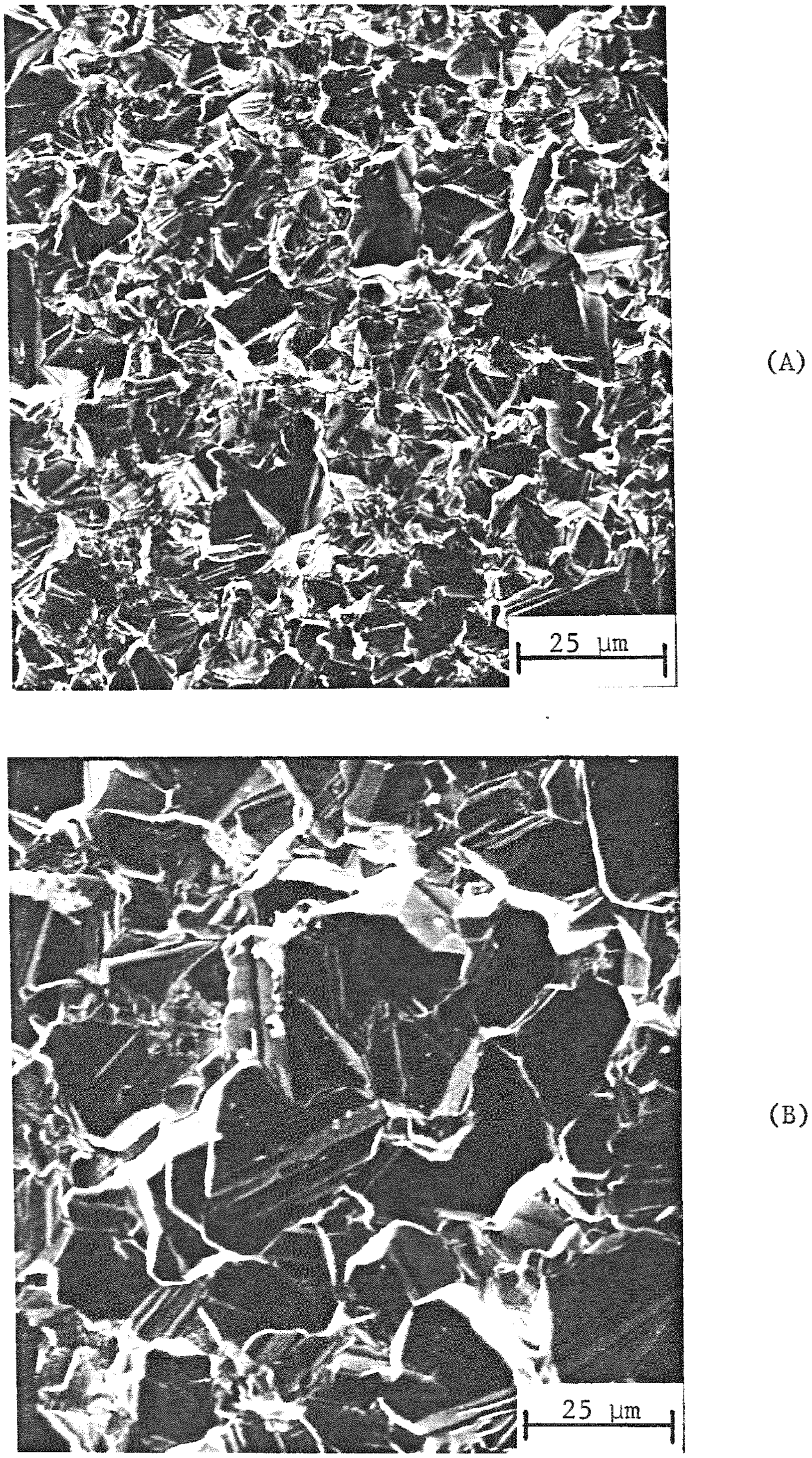

Fig. 6 Scanning electron micrograph of gallium arsenide films deposited on tungsten/graphite substrates at 725°C using $AsH_3/HC\ell$ molar ratios of (A)0.5 and (B)2.

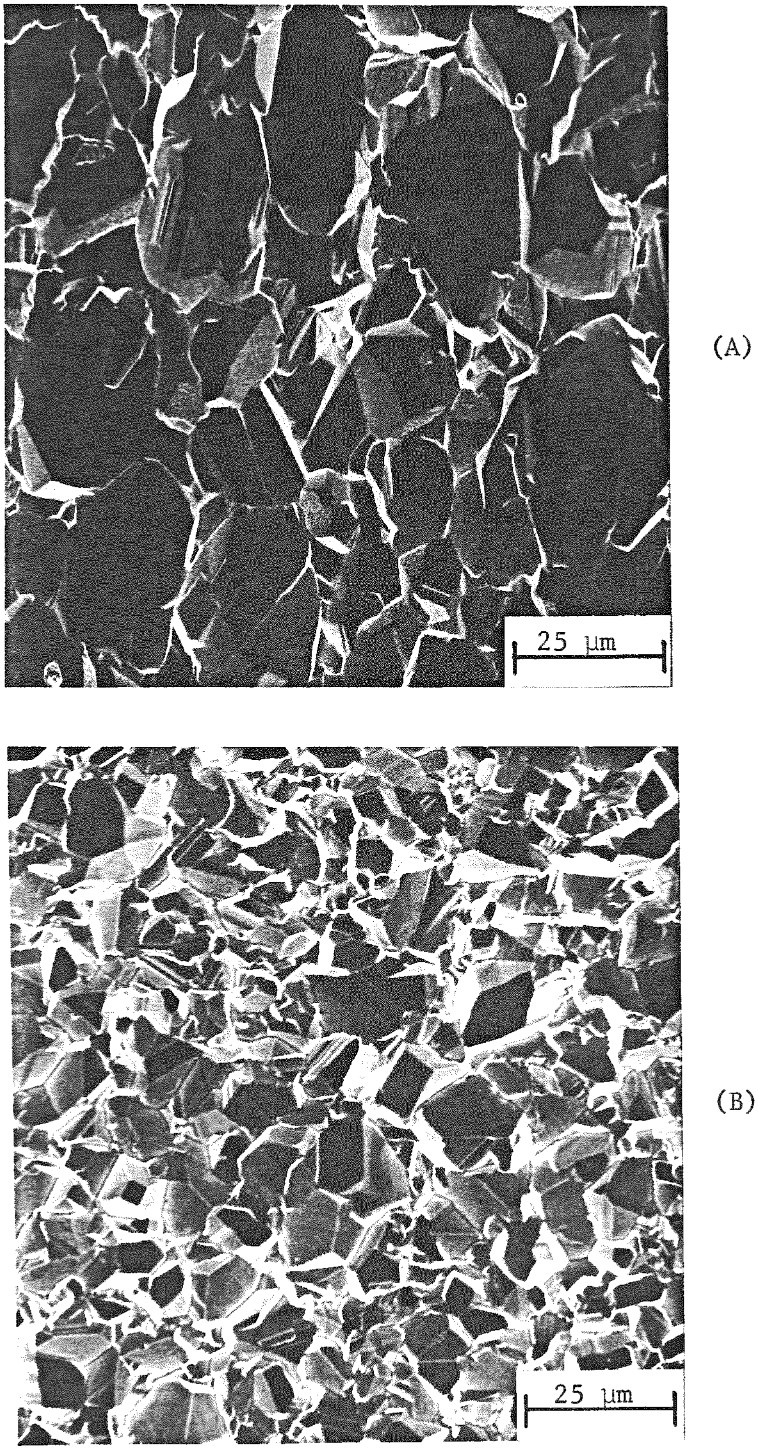

Fig. 7 Scanning electron micrograph of gallium arsenide films deposited on tungsten/graphite substrates using a $AsH_3/HC\ell$ molar ratio of 0.5, (A) at 775°C and (B) at 825°C.

deposited at 725°C, the relative intensities of {111}, {220}, and {311} were found to depend strongly on the $AsH_3/HC\ell$ molar ratio in the reactant mixture. Figures 8A and 8B show the diffraction spectra of gallium arsenide films deposited by using $AsH_3/HC\ell$ molar ratios of 0.5 and 2, respectively. While the film deposited with a low $AsH_3/HC\ell$ molar ratio shows a strong {110} preferred orientation, that deposited at a high $AsH_3/HC\ell$ molar ratio shows a {111} preferred orientation. At higher substrate temperatures, no significant preferred orientations were observed, and the deposited films are essentially polycrystalline. Figure 8C shows the diffraction spectrum of a gallium arsenide film deposited at 775°C. The lack of preferred orientations in gallium arsenide films deposited at high temperatures is presumably related to the chemical reversibility of the deposition reaction.

IV.3. Carrier Concentration in Gallium Arsenide Films

Gallium arsenide films deposited on tungsten/graphite substrates without intentional doping are all n-type. The carrier concentrations in these films were determined at room temperature by the differential capacitance method. An array of sixteen silver dots of about 0.5 mm diameter, 6 - 7 mm apart, were evaporated onto each gallium arsenide film through a metal mask. (Gold-gallium arsenide Schottky barriers prepared by the electroplating technique were found to have very high leakage currents, and no reproducible capacitance-voltage data could be obtained.) The capacitance of these Schottky barriers was measured as a function of the reverse bias, and the dopant concentration in the gallium arsenide film under each Schottky barrier was calculated from the specific differential capacitance. The average dopant concentration and its standard deviation

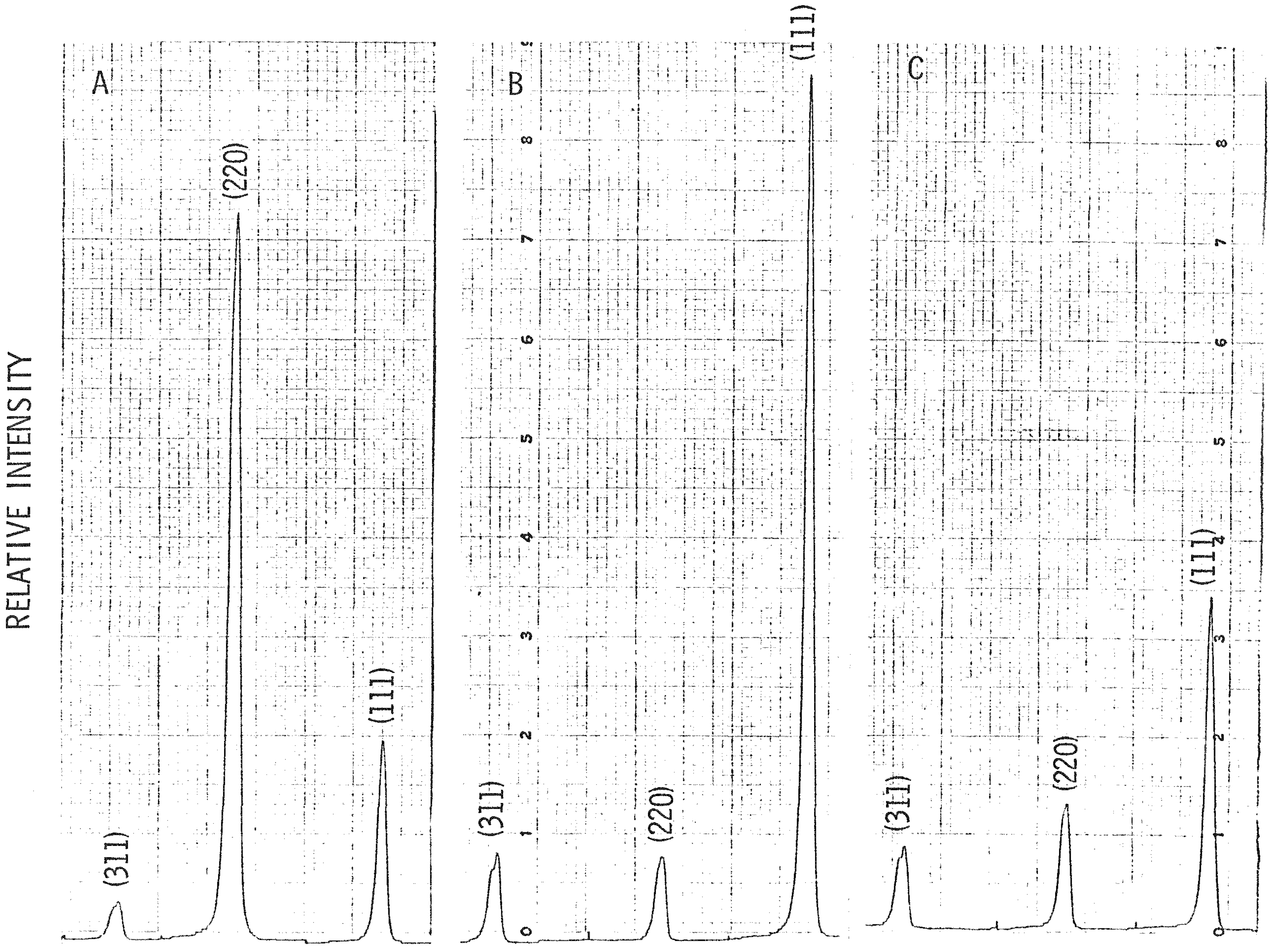

Fig. 8 X-ray diffraction spectra of gallium arsenide films deposited on tungsten/graphite substrates (A) at 725°C and an AsH$_3$/HCℓ molar ratio of 0.5, (B) at 725°C and an AsH$_3$/HCℓ molar ratio of 2, and (C) at 775°C and an AsH$_3$/HCℓ molar ratio of 2.

in each gallium arsenide film was then deduced from the dopant concentrations calculated from the sixteen Schottky barriers. The results are shown in Table I (no meaningful data were obtained for gallium arsenide films deposited on tungsten/graphite at 725°C because of the non-ohmic interface).

Table I. Carrier concentration in gallium arsenide films (x 10^{-16})

$AsH_3/HC\ell$ / Temp., °C	0.5	1.0	1.5	2.0
750	7.8 ± 2	13 ± 6.5	11 ± 1.4	9 ± 0.9
775	7.5 ± 2	5.3 ± 1.8	3.8 ± 0.7	2.3 ± 0.2
800	30 ± 14	12 ± 1.7	8 ± 1.4	7.2 ± 1.6

While the carrier concentration in undoped homoepitaxial gallium arsenide films is approximately 10^{14} cm^{-3}, the carrier concentration in gallium arsenide films on tungsten/graphite substrates is two to three orders of magnitude higher. This high carrier concentration is due presumably to the incorporation of tungsten into gallium arsenide films; gallium arsenide films deposited on substrates with tungsten coating on both sides have higher carrier concentrations. It is seen from Table I that the carrier concentration in each gallium arsenide film is generally uniform within 50%. At a substrate temperature of 750°C, the carrier concentration is essentially independent of the reactant composition. At higher temperatures, the carrier concentration increases with decreasing $AsH_3/HC\ell$ molar ratio due presumably to the contributions of arsenic vacancies.

IV.4. Ohmic Contacts for Gallium Arsenide Films

A low resistance ohmic contact is required for the characterization of gallium arsenide films and the operation of their devices. At present, all gallium arsenide devices are made from single crystals, and ohmic contacts for single crystalline gallium arsenide have been studied by many investigators. Several metals, such as tin, indium, etc., and some alloys have been found to form acceptable contacts to single crystalline gallium arsenide. However, no information is available regarding ohmic contacts for polycrystalline films of gallium arsenide.

The formation of low resistance ohmic contacts to a fine polycrystalline gallium arsenide film of relatively low carrier concentration is difficult due presumably to the oxide associated with its large surface area. Several well-established techniques for the formation of ohmic contacts to single crystalline gallium arsenide were investigated in detail, and the results are summarized below.

Tin is the most widely used contact for gallium arsenide.(35) A simple low temperature alloying process has been developed in which tin spheres are alloyed into bulk n-type gallium arsenide at temperatures between 300° and 450°C in an ambient of argon, hydrogen, and hydrogen chloride.(36) To extend this technique to polycrystalline gallium arsenide films on tungsten/graphite substrates, a conventional chemical vapor deposition apparatus was used. Chemically etched tin or tin-indium spheres were placed on the surface of a gallium arsenide/tungsten/graphite specimen on a graphite susceptor in a horizontal fused silica tube. A chromel-alumel thermocouple was inserted into the interior of the susceptor to monitor its temperature. After purging the reaction tube with hydrogen, a hydrogen-hydrogen chloride mixture containing 5-25% hydrogen chloride was introduced into the reaction tube at a rate of 1 ℓ/min, and the specimen was heated at 250-500°C for 2-10 min. At hydrogen chloride concentrations below about 5% and heating time less than 2 min, wetting was usually not achieved. The use of high concentrations of hydrogen chloride and longer heating time greatly prompted the wetting process. The dark current-voltage characteristics between two tin contacts or between one tin contact and the graphite substrate were used to determine the properties of the contacts. The results indicate that the contacts are either rectifying or have penetrated through the gallium arsenide films.

The use of bulk metals or alloys on gallium arsenide films often leads to the penetration of the molten contact material through the film during heat treatment, presumably along grain boundaries. To minimize this problem, several alloys were evaporated through metal masks onto the surface of polycrystalline gallium arsenide films followed by heat treatment in a hydrogen atmosphere. The use of films of several alloys as ohmic contacts to single crystalline gallium arsenide has been reported by many investigators. For example, a silver-indium-germanium alloy and a silver-indium-zinc alloy have been used for n- and p-type gallium arsenide, respectively.(37) The feasibility of using these alloys as ohmic contacts for polycrystalline gallium arsenide films was investigated. An alloy of 90% (weight) silver, 5% indium, and 5% germanium was prepared by melting the elements in a graphite crucible in a hydrogen atmosphere and was applied to n-type gallium arsenide films by evaporation through a metal mask. The heat treatment was carried out at 630°C for 20 min. in a hydrogen atmosphere. The dark current-voltage characteristics between several contacts and the substrate and those between several pairs of contacts indicate that all contacts are rectifying. Figure 9 shows an example of the current-voltage characteristics between one pair of contacts on an n-type gallium arsenide film with a carrier concentration of about 10^{17} cm^{-3} after heat treatment. A silver (80%)-In(10%)-Zn(10%) alloy was also prepared and applied to p-type gallium arsenide films by evaporation followed by annealing at 630°C. All contacts were also found to be rectifying.

Alloys of gold-germanium have often been used as an ohmic contact to n-type single crystalline gallium arsenide.(38) An eutectic alloy of gold-germanium (about 12% germanium by weight) was prepared from the elements and applied to n-type gallium arsenide films with carrier concentrations of 10^{17} to 10^{18} cm^{-3} by evaporation through metal masks. The heat treatment was carried out in hydrogen at 350-450°C for 1-20 min. All contacts on films with a carrier concentration of about 10^{17} cm^{-3} were found to be rectifying, and contacts on films with a carrier concentration of about 10^{18} cm^{-3} appeared to be ohmic at low voltages.

The difficulties encountered in the formation of ohmic contacts on polycrystalline gallium arsenide films were thought to be related to the oxide associated with the large surface area of fine polycrystalline films. Since the Ag-In-Ge or Au-Ge alloys are relatively inert chemically, the use of a more reactive component in the alloy is desirable for the reduction of the surface oxide. Aluminum is chemically reactive, and its oxide is more stable than gallium and arsenic oxides. The aluminum-germanium eutectic (about 53% germanium by weight with a melting point

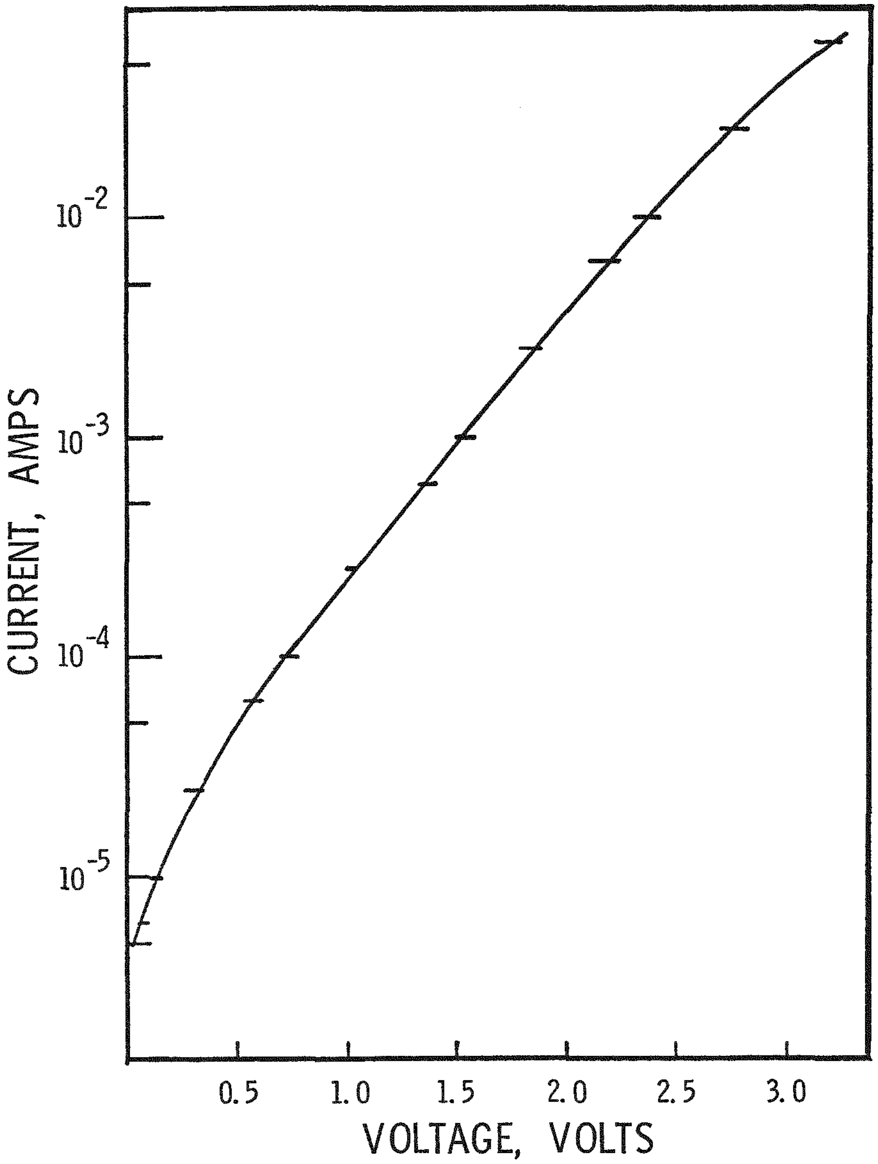

Fig. 9 Current-voltage characteristics between one pair of Ag-In-Ge contacts on an n-type gallium arsenide film with a carrier concentration of approximately 10^{17} cm^{-3} after heat treatment at 630°C.

of about 432°C was prepared from the elements by the melting technique. About 3 μm of the eutectic was evaporated onto n-type gallium arsenide films with carrier concentrations of 10^{17} cm^{-3} on tungsten/graphite substrates. The heat treatment was carried out in a hydrogen atmosphere at 450°C. Although the gallium arsenide surface was uniformly wetted by the eutectic, the resulting contacts were non-ohmic with very high resistance.

The use of thin films of aluminum-germanium eutectic and tin as ohmic contacts for doped gallium arsenide films (carrier concentration: about 10^{18} cm^{-3}) was also investigated. The heat treatment was carried out in a hydrogen atmosphere at 400-450°C for 5-10 min. Although the formation of ohmic contacts to doped semiconductors is generally easier, the results with doped gallium arsenide films were erratic. Attempts were made to apply a capacitor discharge between one pair of contacts. Ohmic contacts appeared to be obtained in a few instances from current-voltage measurements; however, the results were irreproducible, and the contact material penetrated through gallium arsenide films in many cases.

IV.5. Schottky Barriers and Solar Cells

Many metals form Schottky barriers on gallium arsenide crystals. In this work, Schottky barriers were prepared on polycrystalline gallium arsenide films on tungsten/graphite substrates by the evaporation of the barrier metal, gold, silver, or aluminum, through a metal mask under a pressure of less than 10^{-6} Torr. The dark current-voltage characteristics of a number of Au/GaAs Schottky barriers of about 0.5 mm diameter have been measured at room temperature. An example is shown in Fig. 10A, where the gallium arsenide was deposited without intentional doping, and the

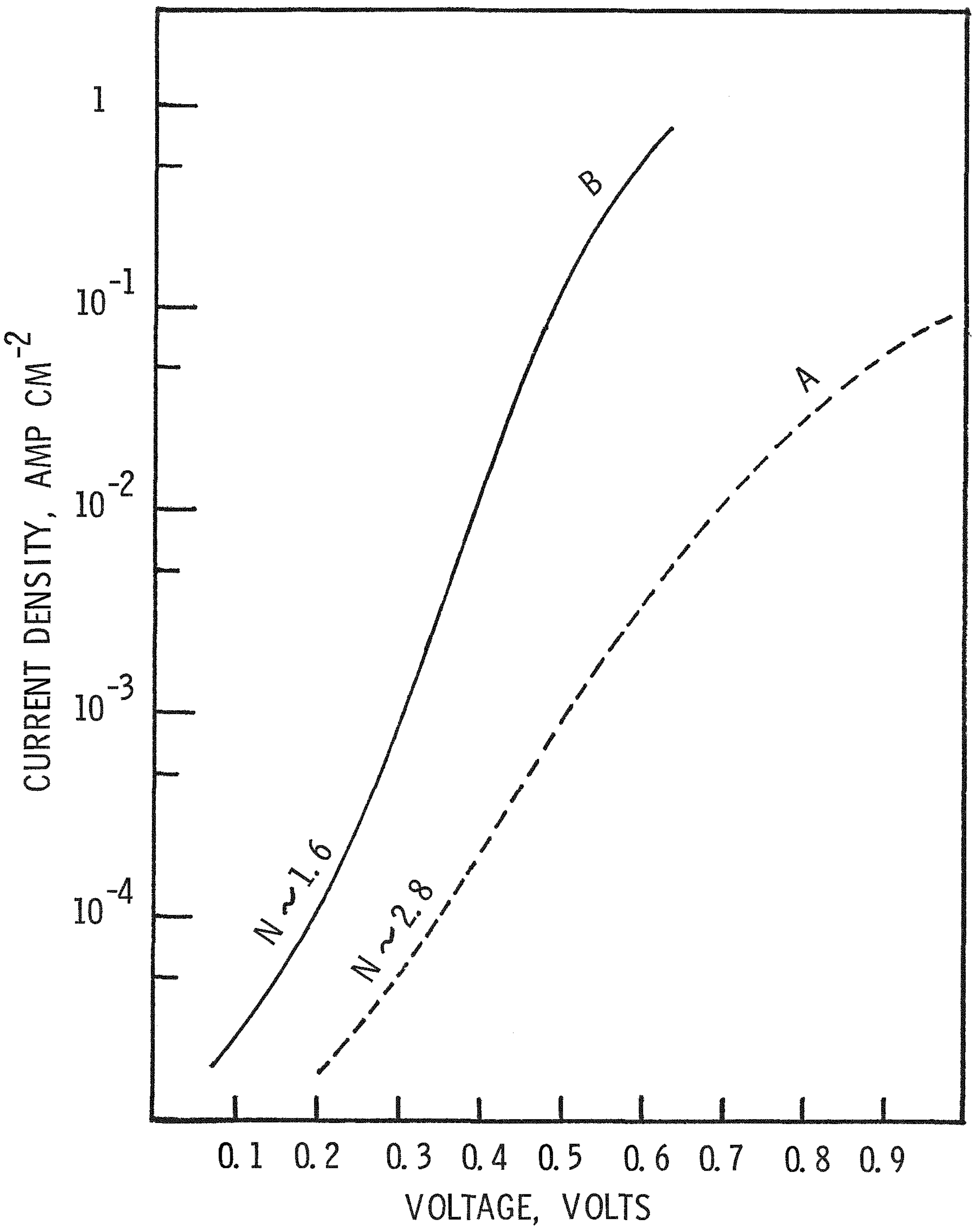

Fig. 10 Dark current-voltage characteristics of (A) Au/n-GaAs/tungsten/graphite and (B) Au/n-GaAs/n^+-GaAs/tungsten/graphite Schottky barriers.

electron concentration was about 10^{17} cm^{-3}. Nearly all diodes have a large empirical "n" factor, higher than 2.5, and a high series resistance. This high series resistance is due to the gallium arsenide/tungsten interface resistance and is a contributing factor to the large "n" value. The series resistance can be reduced substantially by using a heavily doped gallium arsenide (electron concentration about 10^{19} cm^{-3}) interlayer, as shown in Fig. 10B. The characteristics of silver and aluminum Schottky barriers are shown in Figs. 11 and 12, respectively. In both cases, the use of a heavily doped interlayer has reduced substantially the series resistance of the device. However, all diodes have relatively high saturation currents, about 10^{-6} A/cm^2. Figure 13 shows the capacitance-voltage characteristics of gold and silver Schottky barriers under reverse bias. The barrier heights calculated from the intercept on the voltage axis and the Fermi energy are approximately 1.05 and 0.99 eV for Au/n-GaAs and Ag/n-GaAs, respectively.

A number of Schottky barrier solar cells of 4-8 cm^2 area have been prepared from gallium arsenide films on tungsten/graphite substrates. To reduce the series resistance associated with the n-GaAs/W interface, a heavily doped interface layer was used. Thus, the n-GaAs/n^+-GaAs/W/graphite structures were prepared for the fabrication of solar cells. The carrier concentration in the n-GaAs is approximately 10^{17} cm^{-3}. Furthermore, the deposited gallium arsenide films were oxidized in situ at 200°C to produce a thin oxide film, since fine polycrystalline gallium arsenide films oxidized readily in air and the oxide formed in this manner may not be uniform. To prepare the solar cell, a gold or silver film of 60-70 Å

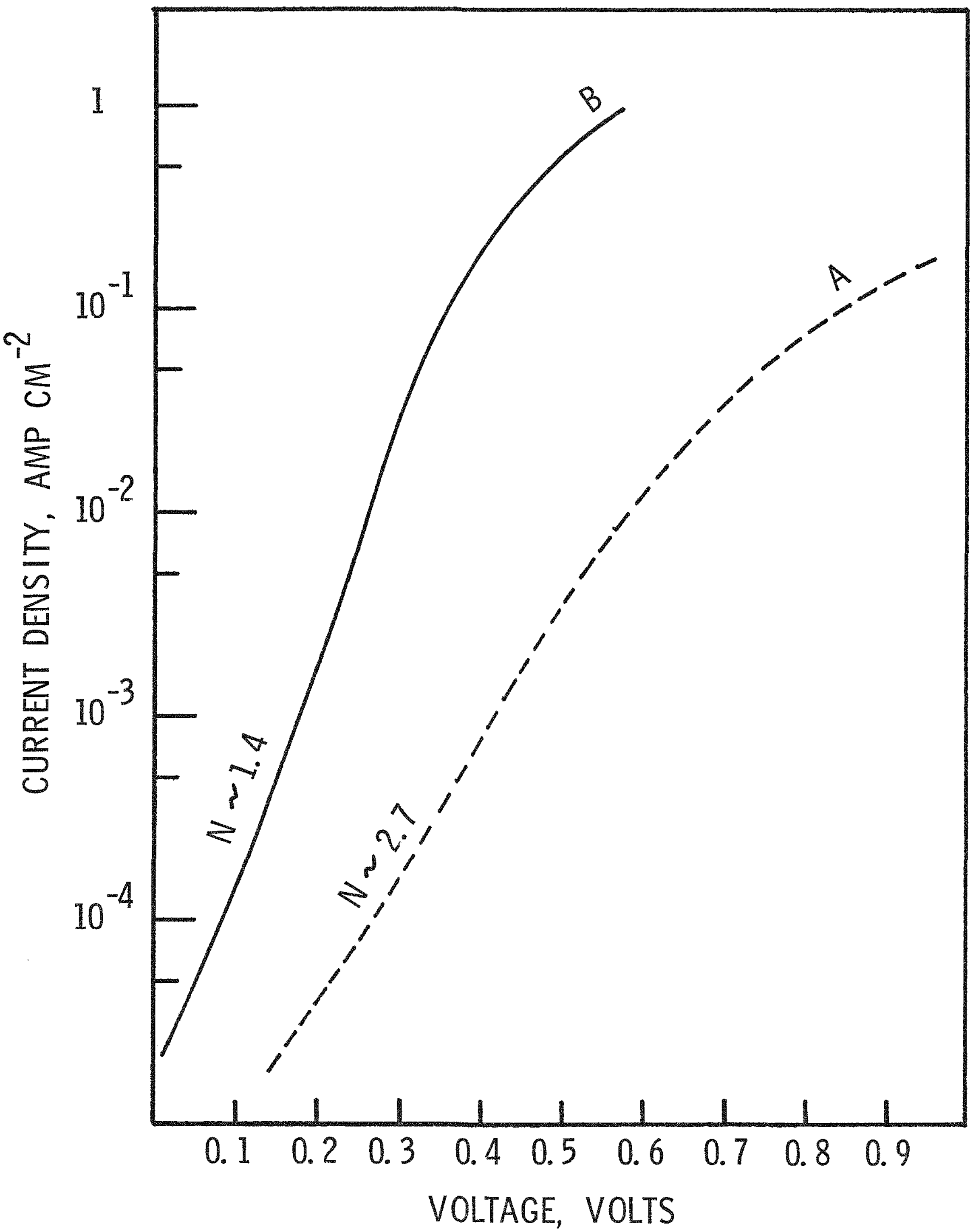

Fig. 11 Dark current-voltage characteristics of (A) Ag/n-GaAs/tungsten/graphite and (B) Ag/n-GaAs/n$^+$-GaAs/tungsten/graphite Schottky barriers.

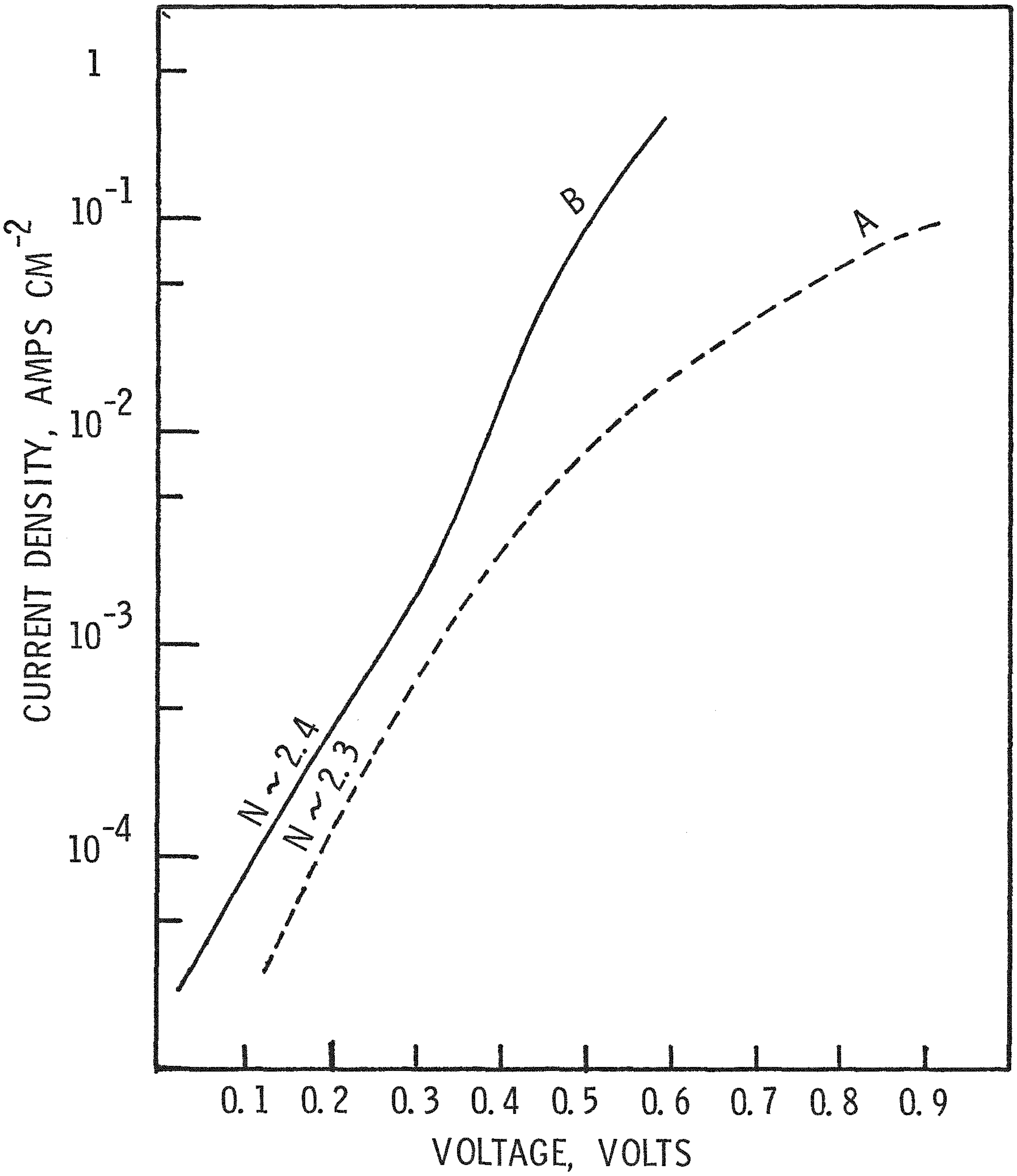

Fig. 12 Dark current-voltage characteristics of (A) Al/n-GaAs/tungsten/graphite and (B) Al/n-GaAs/n^+-GaAs/tungsten/graphite Schottky barriers.

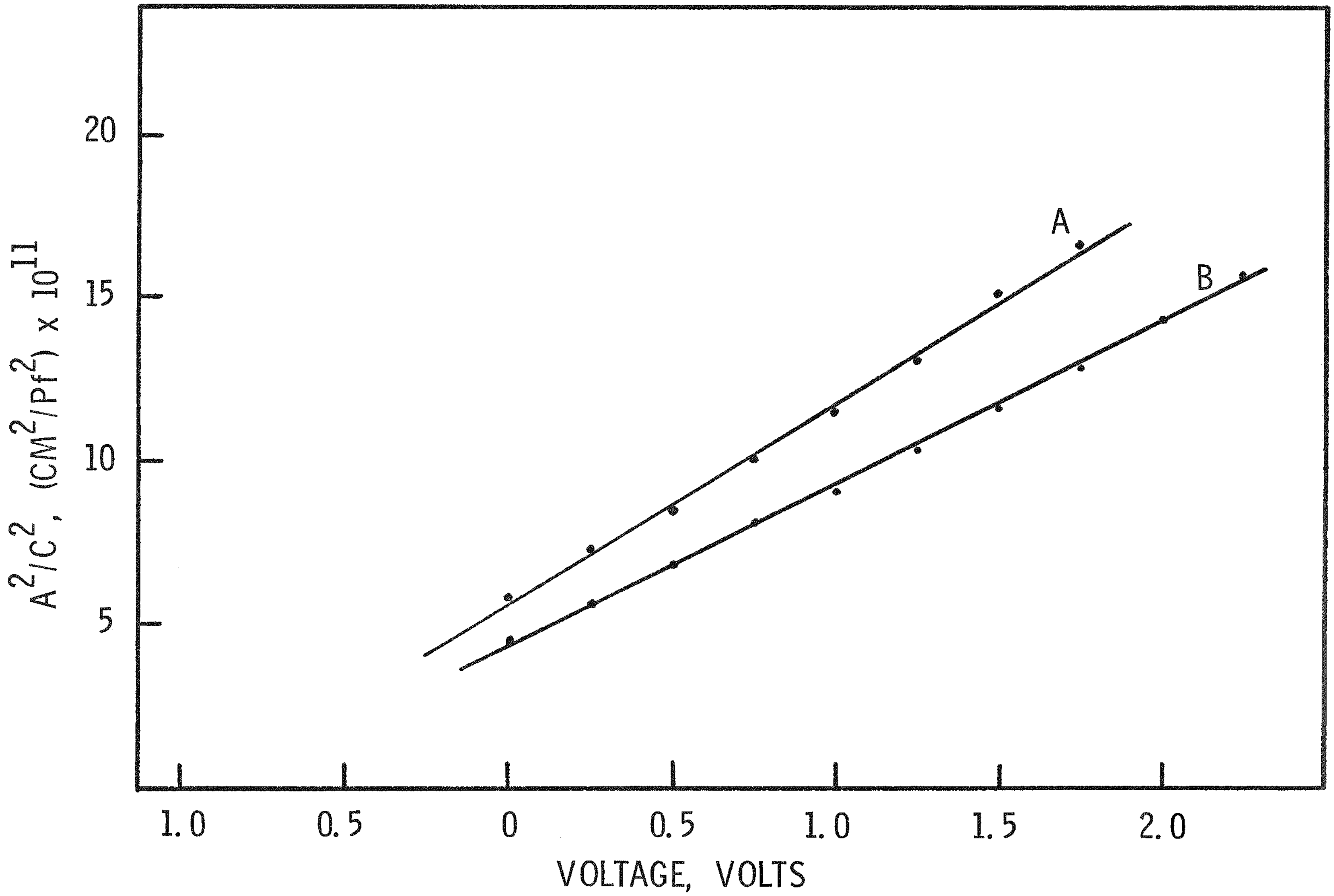

Fig. 13 Capacitance-voltage characteristics of (A) a gold/n-gallium arsenide and (B) a silver/n-gallium arsenide Schottky barrier under reverse bias.

was evaporated onto the surface of gallium arsenide, and the grid contact was formed by evaporation through a mask.

The current-voltage characteristics of the solar cells were measured at room temperature in the dark and under illumination with ELH quartz-halogen lamps calibrated with standard silicon solar cells at AM1 conditions. Figure 14 shows an example of the dark current-voltage characteristics of a solar cell of about 6.3 cm^2 area. In the forward direction, the empirical "n" factor is about 1.8, and the reverse current is about 10^{-5} Amp/cm^2 at 0.5 V. Figure 15 shows the current-voltage characteristics of this cell under illumination. The open-circuit voltage, short-circuit current density, and fill factor are 455 mV, 12.5 mA/cm^2, and 60%, respectively, corresponding to an AM1 efficiency of about 3.4%. The series resistance of this solar cell was measured to be 0.48 ohms. The improvement in conversion efficiency is due mainly to the reduced series resistance associated with the use of the n^+-GaAs interface layer.

The spectral response of several thin film gallium arsenide solar cells were measured by using a calibrated single crystalline silicon solar cell as a reference. The calibrated cell was 2 cm x 2 cm in area, and the active area of the gallium arsenide solar cell was made to the same size by masking. The spectral response of gallium arsenide solar cells is generally poor. An example is shown in Fig. 16, where the spectral response of a gallium arsenide cell is compared with that of a calibrated silicon cell.

The barrier height in a number of Au/n-GaAs thin film cells has been measured by the photoresponse technique. The apparatus consists of a source of monochromatic light, a light detector with known spectral

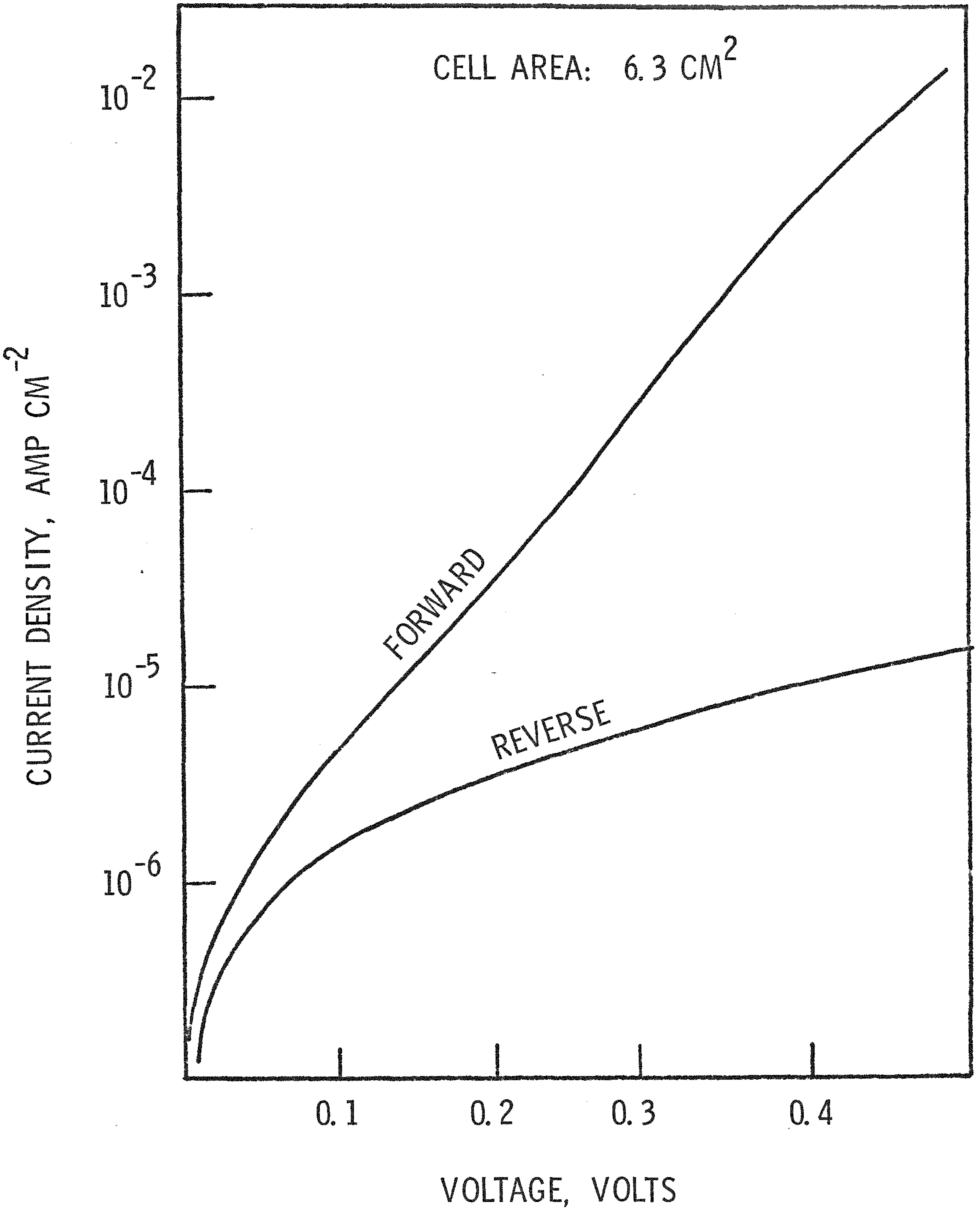

Fig. 14 Dark current-voltage characteristics of a thin film gallium arsenide Schottky barrier solar cell of 6 cm^2 area.

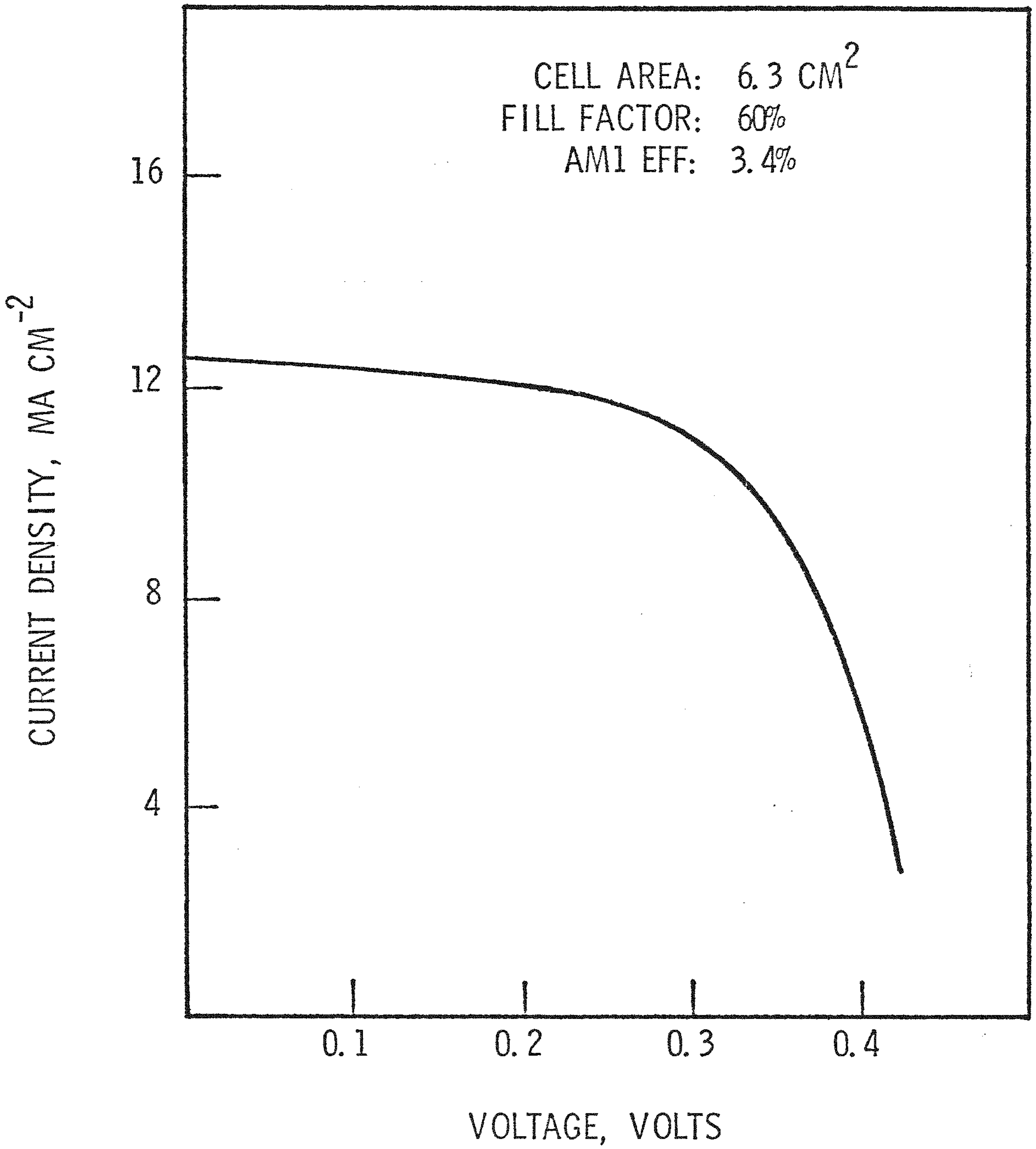

Fig. 15 Current-voltage characteristics of the solar cell shown in Fig. 14 under illumination with ELH quartz-halogen lamps equivalent to AM1 conditions.

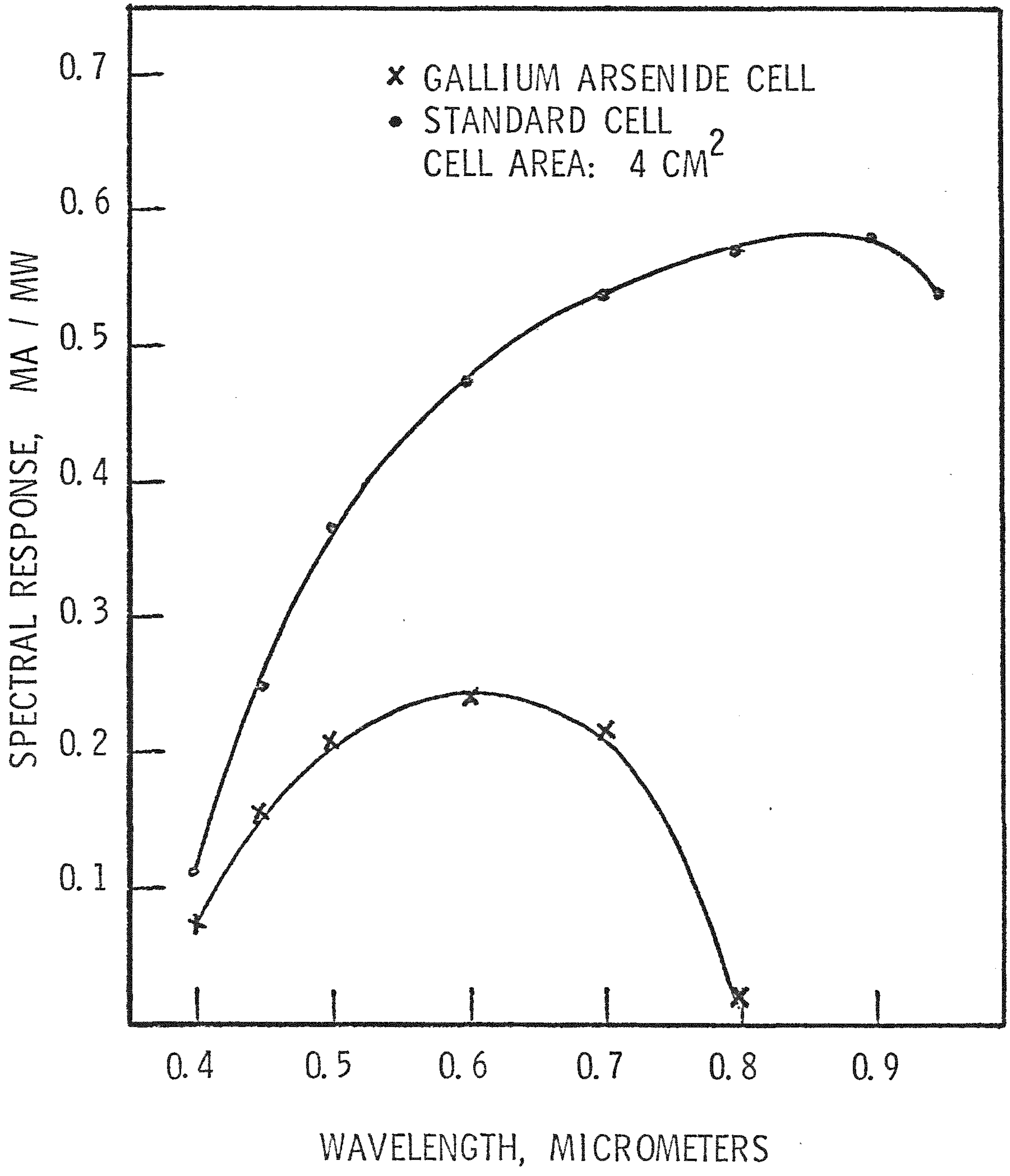

Fig. 16 Spectral response of a thin film gallium arsenide solar cell (without AR coating) in comparison with a calibrated single crystalline silicon solar cell.

response, and a lock-in amplifier for measuring the output of the solar cell. At photon energies less than about 1.1 eV, the signal was usually less than 10 μV and showed no appreciable change with decreasing photon energy. An example of the photoresponse data is shown in Fig. 17, where the square root of photoresponse versus photon energy relation is reasonably linear in the energy range of 1.12-1.24 eV. The barrier height in this cell obtained from the least square fit is 0.99 eV, and that measured for a number of other cells is in the range of 0.9-1.04 eV. As a comparison, the barrier heights of gold on single crystalline gallium arsenide of {100} and {111} orientations are 0.90-0.94 eV.

The spectral response in thin film gallium arsenide solar cells was also used for the measurement of the minority carrier diffusion length in gallium arsenide films. The spectral response of the cell was measured at 7000 and 7500 Å. The ratio of the measured responses is related to the minority carrier diffusion length in the gallium arsenide film. By comparing this ratio with the ratios calculated as a function of diffusion length for materials of the same dopant concentration,(39) the diffusion length in the gallium arsenide film can be deduced. Most of the gallium arsenide films were found to have a diffusion length of 0.2-0.7 μm.

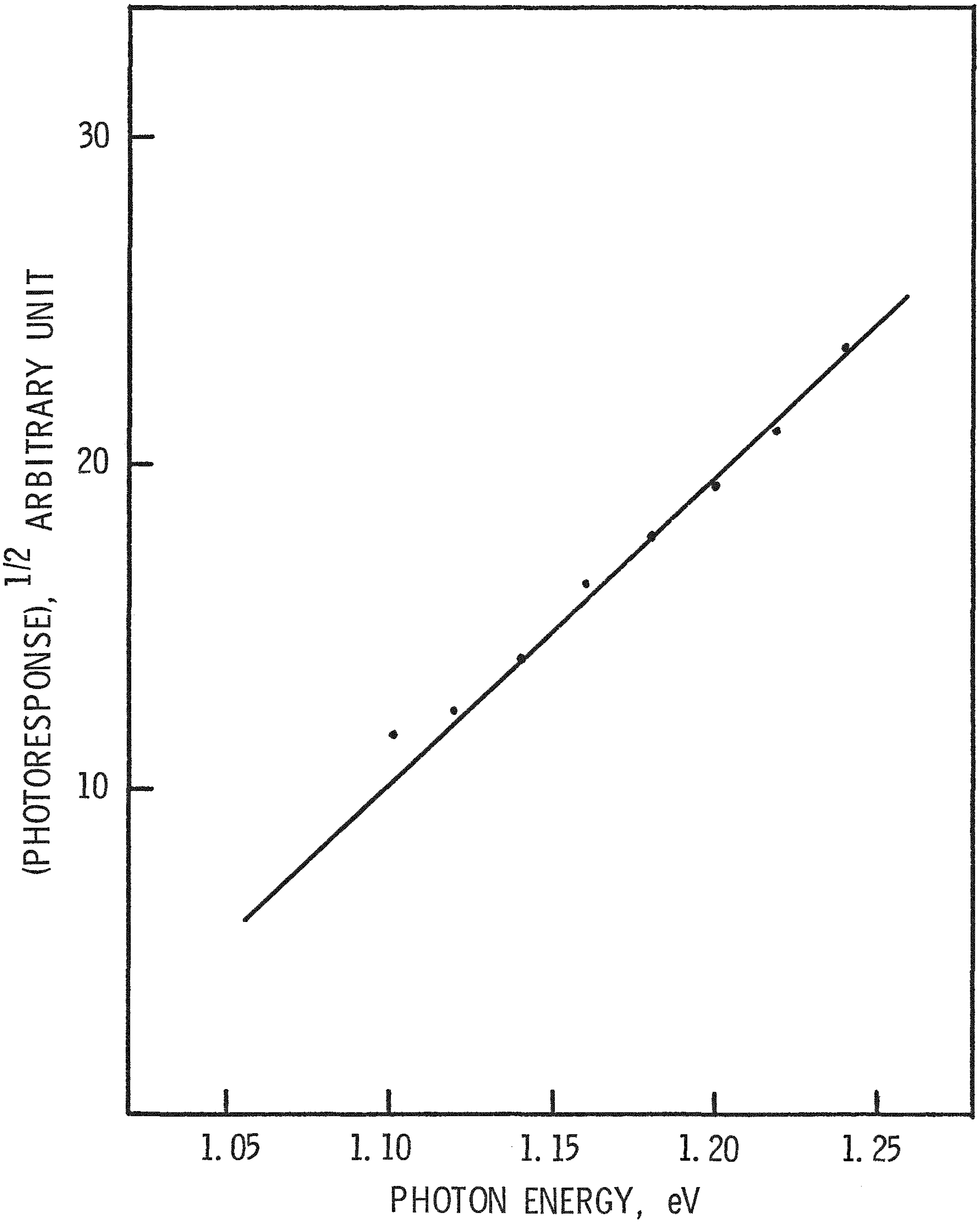

Fig. 17 The photoresponse of a thin film gallium arsenide Schottky barrier solar cell as a function of photon energy.

V. Gallium Arsenide Films on Germanium (Recrystallized)/Tungsten/Graphite Substrates

Gallium arsenide films deposited on tungsten/graphite substrates consist of relatively small crystallites, less than 20 μm, due to the polycrystalline nature of tungsten. To increase substantially the crystallite size in gallium arsenide films, recrystallized germanium films on tungsten/graphite were used as substrates for the deposition process.

V.1. Properties of Gallium Arsenide Films

Gallium arsenide films were deposited on p-germanium/n-germanium(recrystallized)/tungsten/graphite substrates without intentional doping. The experimental conditions were similar to those used for the heteroepitaxial growth of gallium arsenide on single crystalline germanium substrates (cf. Section II.4). The temperatures of the substrate and gallium were 740 and 900°C, respectively, and the flow rates of hydrogen, hydrogen chloride, and arsine were 2 ℓ/min, 15 mℓ/min, and 45 mℓ/min, respectively. The deposition rate was approximately 0.4 μm/min, somewhat lower than the deposition rate of gallium arsenide on single crystalline germanium of {100} orientation. The gallium arsenide films deposited on germanium(recrystallized)/tungsten/graphite substrates have dendritic structure similar to the substrate in appearance, and show a strong {111} preferred orientation as indicated by X-ray diffraction studies. Figure 18 shows the scanning electron micrograph of an as-deposited surface of gallium arsenide, where the crystallites are several hundred micrometers in length. The mechanically polished and chemically etched surface of the vertical

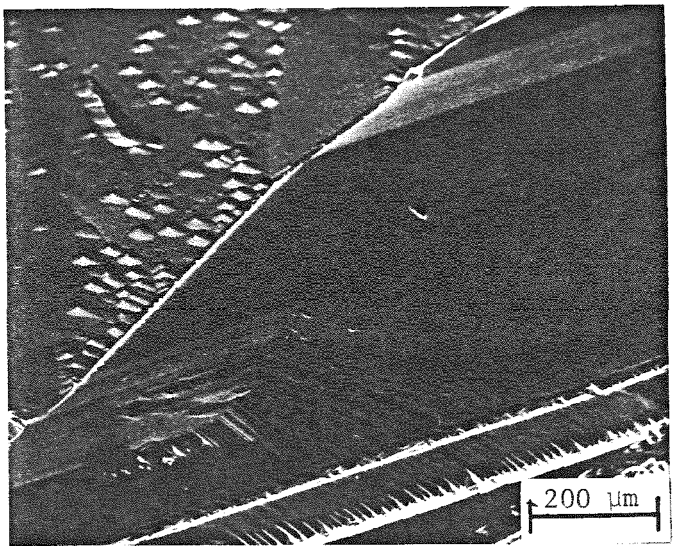

Fig. 18 Scanning electron micrograph of a gallium arsenide film deposited on a germanium(recrystallized)/tungsten/graphite substrate.

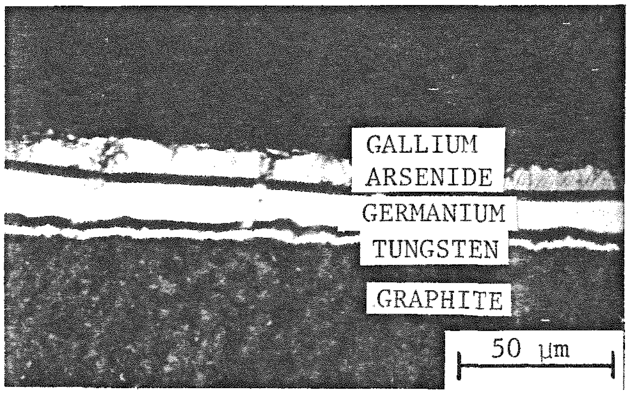

Fig. 19 Mechanically polished and chemically etched surface of the vertical cross section of a gallium arsenide film on germanium(recrystallized)/tungsten/graphite substrate.

cross section of a specimen is shown in Fig. 19, where the deposited gallium arsenide films appears to be epitaxial with respect to the substrate.

The resistivity of, and Hall mobility in, a number of gallium arsenide films deposited on p-germanium/n-germanium(recrystallized)/tungsten/graphite substrates were measured at room temperature by the van der Pauw technique. Considerable variations were observed, and better films were found to have Hall mobilities of 400-700 cm^2/V-sec and carrier concentrations of (2-4) x 10^{17} cm^{-3}.

P-type gallium arsenide films with net carrier concentrations in the range of 10^{16} - 5 x 10^{18} cm^{-3} have been prepared by using zinc as a dopant. The amount of zinc incorporation was controlled by the temperature of zinc source and the flow rate of hydrogen.

V.2. Solar Cell Characteristics

A series of experiments have been carried out to prepare p-n junctions and Schottky barrier solar cells from gallium arsenide films deposited on germanium(recrystallized)/tungsten/graphite substrates. Since gallium arsenide films deposited on recrystallized germanium films are always of n-type conductivity, the junctions were of the p^+n configuration. They were prepared by depositing successively about 15 μm of gallium arsenide film without intentional doping and 0.5 μm of zinc-doped film (carrier concentration: about 10^{18} cm^{-3}). The dark current-voltage characteristics of a p^+-n junction of about 1 mm diameter, measured by using a gallium-indium contact on the p^+ surface, are shown in Fig. 20. In the forward direction, the "n" value in the diode equation is about 2.3, and a high

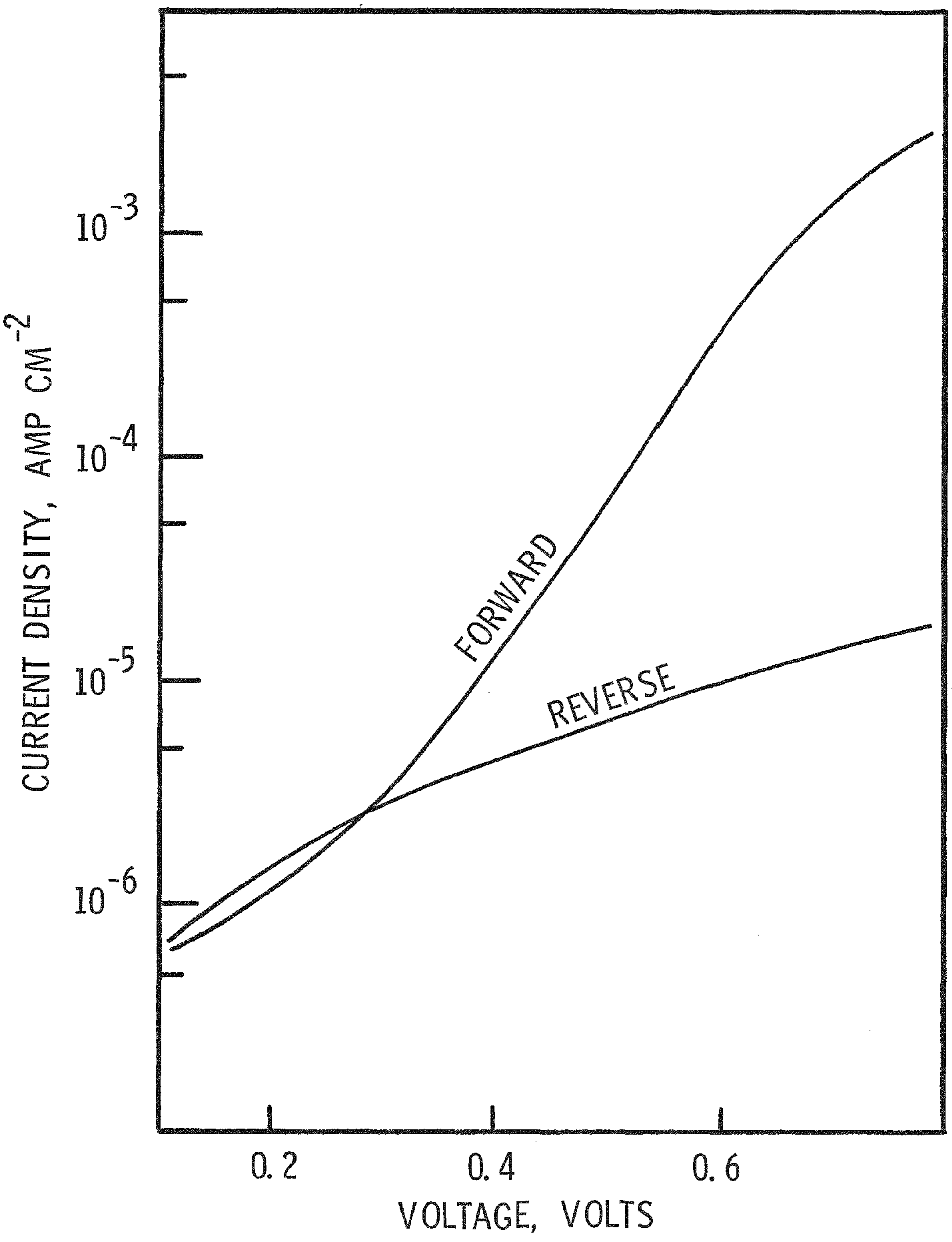

Fig. 20 Dark current-voltage characteristics of a gallium arsenide p^+n junction deposited on a germanium(recrystallized)/tungsten/graphite substrate.

series resistance is also apparent. The reverse current density is very high, about 10^{-5} A/cm^2 at 0.5 V. The open-circuit voltage of this type of solar cell under AM1 conditions is only about 90 mV.

A number of Schottky barrier type solar cells were also prepared from gallium arsenide films with a net carrier concentration in the range of $10^{17} - 4 \times 10^{17}$ cm^{-3}; the films with low carrier concentrations were prepared by using zinc as a dopant during the deposition process. Although the crystallite size in these films is many times larger than that in gallium arsenide films on tungsten/graphite substrates, the current-voltage characteristics and conversion efficiency of solar cells from gallium arsenide films on recrystallized germanium were considerably inferior. Under AM1 conditions, the open-circuit voltage, short-circuit current density, and fill factor of a typical solar cell are 0.27 V, 7 mA/cm^2, and 43%, respectively, corresponding to a conversion efficiency of about 0.8%. The characteristics of Au/GaAs/Ge(recrystallized)/W/graphite solar cells appear to be affected by the crystallite size in the gallium arsenide film. Figures 21A and 21B show the dark forward characteristics of two solar cells, where the average crystallite size in A is considerably smaller than that in B. Both cells are characterized by excessive junction current at low voltage and high series resistance. The open-circuit voltage and short-circuit current density of B are 0.18 V and 9.4 mA/cm^2, respectively, and those of A are 0.14 V and 8 mA/cm^2, respectively. Both cells have low fill factors, about 30%, due to the high series resistance. The high junction current in these devices is due presumably to the high diffusion rate of germanium thru grain boundaries, thus contributing to the shunting.

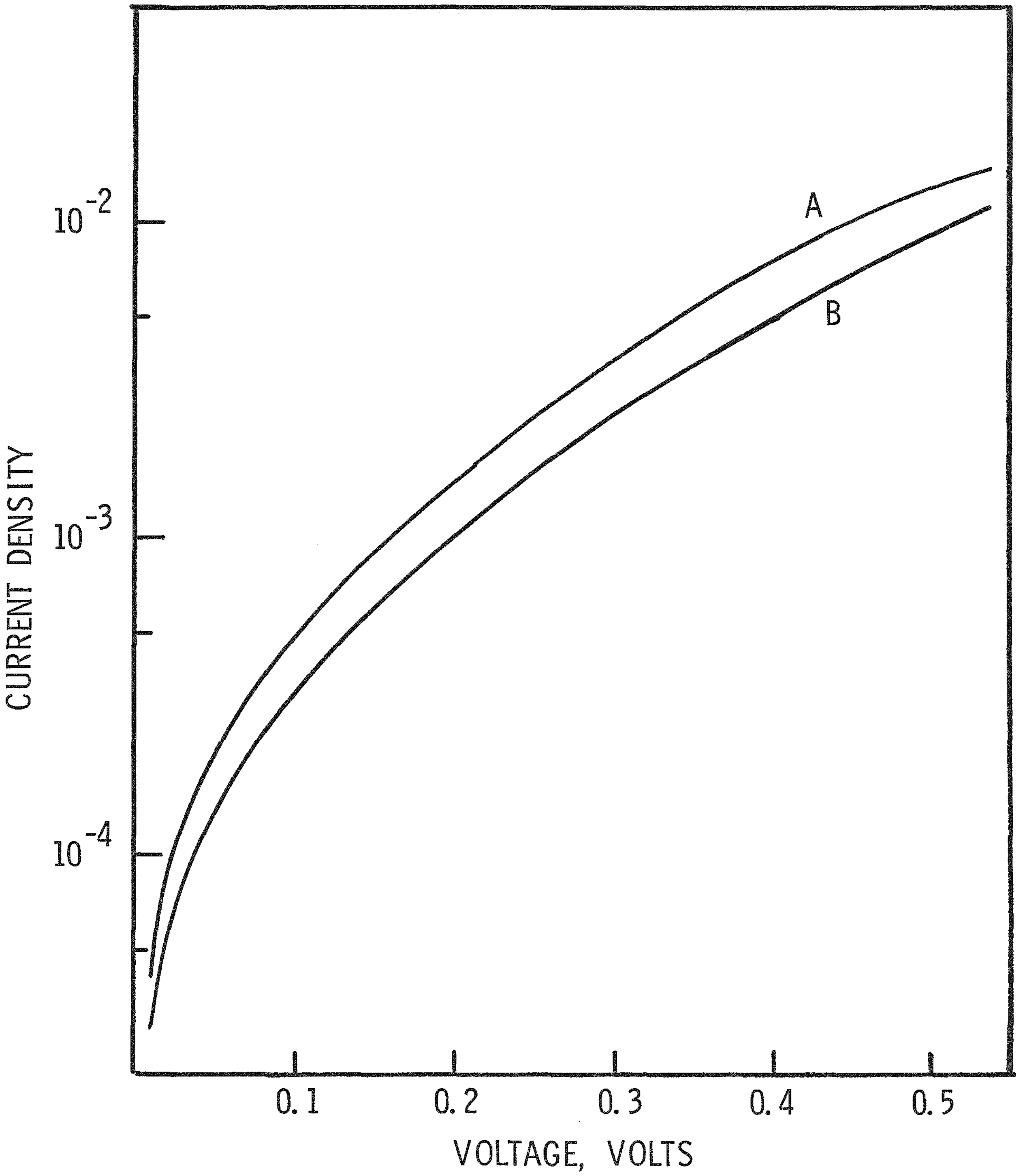

Fig. 21 Dark forward characteristics of two gallium arsenide Schottky barrier solar cells on Ge(recrystallized)/W/graphite substrates. The average crystallite size in A is considerably smaller than that in B.

The high series resistance is related to the GaAs/Ge interface resistance.

To verify the correlation between the high junction current and the diffusion of germanium along grain boundaries, an n-type gallium arsenide film was deposited on a CVD Ge/tungsten/graphite substrate without intentional doping. The dark forward characteristics of a Schottky barrier solar cell from this film are shown in Fig. 22A, where the high junction current and high series resistance are apparent. The open-circuit voltage, short-circuit current density of this cell are 0.02 V and 3 mA/cm^2, respectively. These characteristics are considerably inferior to those of solar cells prepared from gallium arsenide film on tungsten/graphite substrates, indicating that the diffusion of germanium along grain boundaries is a contributing factor to the poor characteristics of Au/GaAs/CVD Ge/W/graphite cells. When a low concentration of zinc was used as a dopant during the deposition of an n-type gallium arsenide film on a CVD Ge/W/graphite substrate, the dark forward characteristics of the solar cell were considerably improved, Fig. 22B. The open-circuit voltage and short-circuit current density of this cell are 0.15 V, and 6.2 mA/cm^2, respectively. Since zinc is known to have a high diffusivity in gallium arsenide, the enhanced diffusion of zinc along grain boundaries compensates the effects of germanium and reduces shunting.

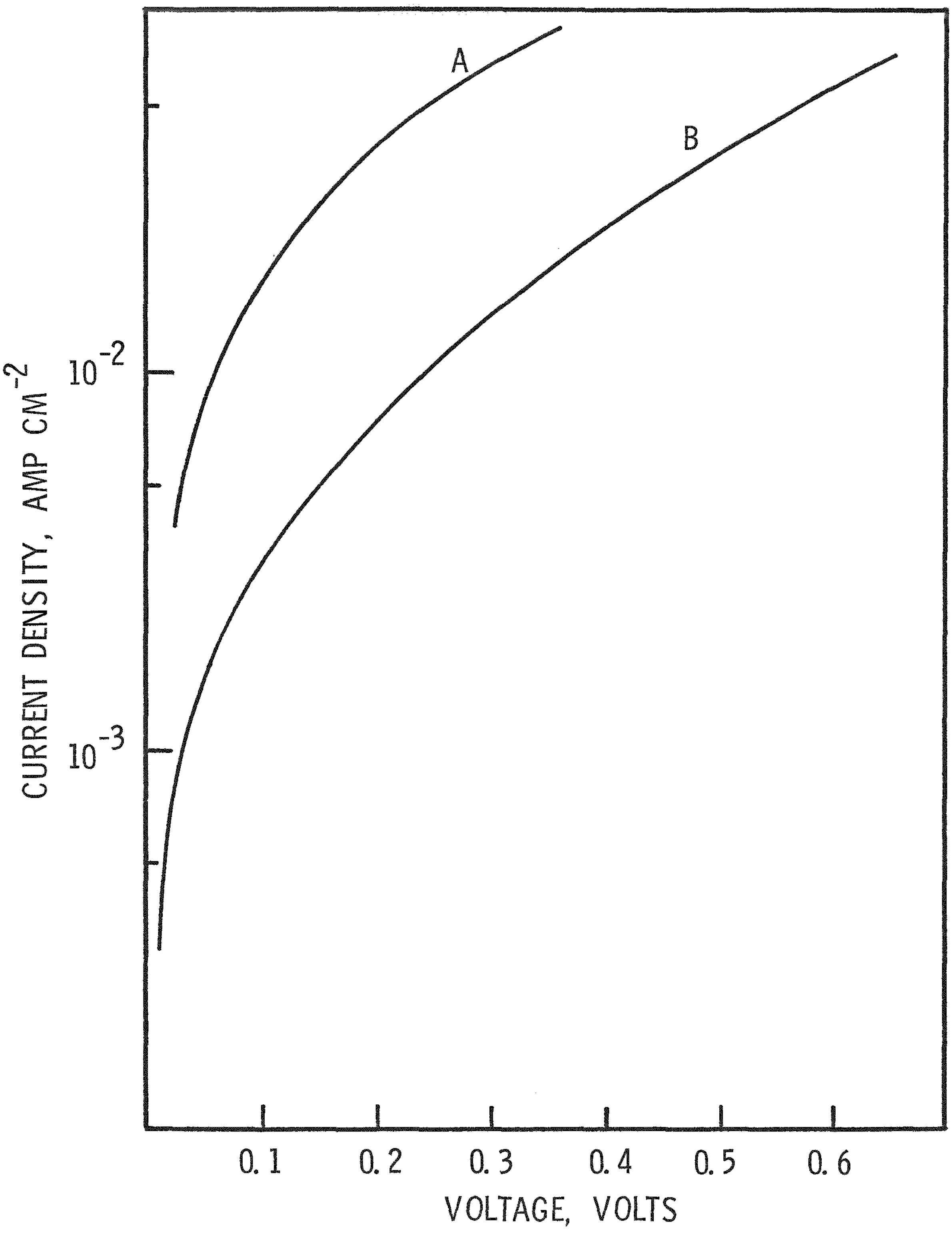

Fig. 22 Dark forward characteristics of (A) undoped gallium arsenide and (B) zinc-doped gallium arsenide solar cells on CVD Ge/W/graphite substrates.

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VII. Conclusions

1. Highly adherent tungsten films can be deposited on graphite at 500°C or higher.
2. Tungsten/graphite is a suitable substrate for the deposition of gallium arsenide films. The microstructural and cyrstallographic properties of, and the carrier concentration in, these films are affected by the substrate temperature and reactant composition. Films deposited under optimum conditions have an average crystallite size of about 15 μm; however, they are essentially polycrystalline.
3. Silver and gold Schottky barriers on n-GaAs/W/graphite structures are not ideal diodes and also exhibit high series resistances. The series resistance can be reduced substantially by using an n^+-GaAs interlayer.
4. MOS type solar cells fabricated from n-GaAs/n^+-GaAs/W/graphite structures have an AM1 efficiency (without antireflection coatings) of up to 3.5%.
5. The formation of ohmic contacts to polycrystalline gallium arsenide films on W/graphite substrates is very difficult.
6. Gallium arsenide/graphite structures have high interfacial resistance.
7. Germanium films deposited on graphite at temperatures below 900°C consist of small crystallites and cannot be recrystallized to produce uniform films because of the low graphite-germanium interfacial tension. Germanium films deposited on tungsten/graphite substrates can be recrystallized to yield large grain films with a strong {111} preferred orientation.
8. Gallium arsenide films deposited on germanium(recrystallized)/W/graphite substrates are epitaxial with respect to the substrate. However,

the gallium arsenide films are contaminated with germanium, and solar cells fabricated from these films have poor characteristics due presumably to the high diffusion rate of germanium along grain boundaries.

VIII. Plan for the Next Year

1. Further optimization of the deposition of gallium arsenide films on tungsten/graphite substrates.
2. Optimization of the configuration and fabrication techniques of thin film gallium arsenide solar cells on tungsten/graphite substrates, including the use of antireflection coatings.
3. Deposition and characterization of gallium arsenide films on graphite substrates by using a heavily doped interface layer to eliminate the contact resistance.
4. Limited investigation on the grain boundary properties in GaAs/Ge(recrystallized)/W/graphite structures.

IX. Publications

IX.1. Oral Presentation

1. "Characterization of Photovoltaic Materials by X-ray Diffraction," presented at the National Meeting of the American Crystallographic Association, Feb. 21-25, 1977, Asilomar, California.
2. "Gallium Arsenide Films on Foreign Substrates," presented at the 115th National Meeting of the Electrochemical Society, May 8-13, 1977, Philadelphia, Pa. Electrochem. Soc. Extended Abstract, 77-1, 274 (1977).
3. "Thin Film Gallium Arsenide Solar Cells," an extended abstract submitted for presentation at the 116th National Meeting of the Electrochemical Society.

IX.2. Scientific Papers

1. "Germanium Films in Graphite Substrates," Thin Solid Films, in press.
2. "Gallium Arsenide Films on Recrystallized Germanium Films," Journal of Applied Physics, in press.
3. "Gallium Arsenide Films on Tungsten/Graphite Substrates," Journal of Electrochem. Soc., submitted for publication.