Device Quality Polycrystalline Gallium Arsenide on Germanium/Molybdenum Substrates

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ABSTRACT

This paper describes the growth of polycrystalline films of gallium arsenide on molybdenum substrates with an intermediate layer of germanium. The gallium arsenide layer is grown by the reaction of trimethylgallium and ar-sine in a cold-wall reactor system. Germanium layers are formed by vacuum evaporation, as well as by the pyrolysis of germane gas. Techniques are de-scribed for minimizing massive autodoping effects which are commonly observed in the heteroepitaxy of these semiconductors. Doping concentrations in the range of $(7-13) \times 10^{15}$ /cm³ are obtained for the gallium arsenide film. Schottky diodes, fabricated in this material, exhibit avalanche breakdown in the range of 30-35V.

Recently, there has been a significant increase of interest in solar cells which use thin semiconducting films, based on economic grounds. Direct-gap semiconductors have a great advantage in this application because of their high absorption coefficient, coupled with a sharp absorption vs. wavelength characteristic. Of these, gallium arsenide is the most promising candidate (1) because it has an optimum energy gap for this application. In addition, the ability to grow device quality, single crystal material has been well established by a number of conventional techniques. There is an excellent chance that this technology can be readily adapted to polycrystalline films (2).

Substrates for these films must have a reasonably good thermal expansion coefficient match to GaAs, and must not be a source of deep impurities. Both tungsten and molybdenum meet these requirements better than other metals, and are suitable candidates. However, substrates using suitable ceramics, glasses, metal laminates, carbon, or graphite, in conjunction with a barrier layer of molybdenum or tungsten, must eventually be used in order to keep down the cost of these cells.

This paper describes work on the development of device quality layers of polycrystalline gallium arsenide, grown by the reaction of trimethylgallium and arsine gas. These layers have been grown on molybdenum substrates because of its somewhat greater ease of handling over tungsten.

It is necessary that the GaAs make good electrical contact with the molybdenum substrate. One solution lies in the use of an intermediate layer of some material such as tin or germanium, both of which result in an n⁺-doped GaAs interface. We have chosen germanium for this layer because of its close lattice match to GaAs. In addition, it makes a good ohmic contact to molybdenum, and both evaporated and chemical vapor deposition (CVD) films adhere well to this substrate. \bar{CVD} germanium has the additional advantage that it can be grown directly in the same reactor as the GaAs, avoiding the use of a separate vacuum evaporation step. In addition, crystal size of both types of germanium films can be controlled by deposition and annealing at high temperatures, with no stoichiometry problems, since it is an elemental semiconductor. Gallium arsenide can be epitaxially grown on this layer because of its excellent lattice match to germanium. This results in improved morphology for the active layer.

A number of workers have commented on the difficulty of obtaining device quality material, with

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electron concentrations below 10^{17} /cm³, by the epitaxy of GaAs on Ge (3-5). This paper outlines the reasons for this difficulty in what is at first glance an extremely simple combination for heteroepitaxy. Device quality layers with electron concentration in the (7-13) imes 10¹⁵ range are demonstrated for the first time.

Experimental Conditions

Apparatus.-The growth of polycrystalline gallium arsenide films was carried out in a conventional rf heated, cold wall reactor of the type described earlier (6). The reactants were introduced into a 50 mm ID, 37 cm long, horizontally positioned quartz reaction chamber containing a pyrolytic graphite-coated graphite susceptor. A baffle was used to mix the reactants prior to their entry into the hot zone. The temperature was monitored using a Pt/Pt-13% Rh thermocouple enclosed in a quartz sheath and inserted into the susceptor, and verified by infrared pyrometric measurements. Gases were delivered to the reaction chamber through stainless steel tubing, except in the case of HCl gas where Monel and Teflon tubing were used to minimize contamination.

Germanium films, made by chemical vapor deposition techniques, were also grown in this reactor. A conventional vacuum evaporator was used in experiments with evaporated germanium layers.

Reactants .- Technical grade hydrogen (99.95% purity) was successively passed through an oxygen-removing catalyst,¹ a molecular sieve,¹ a palladium purifier,¹ and a cold trap at 77°K to obtain the carrier gas used in this investigation. This carrier gas was passed through a stainless steel bubbler containing electronic grade trimethlygallium² (TMG) at 0°C. Germane gas used in this work was a 2% mixture of electronic grade germane (99.998% purity) in six nines hydrogen.^1 The arsine gas used was a $10\,\%$ mixture of electronic grade arsine (99.998% purity) in six nines hydrogen.³ A 1% mixture of electronic grade HCl gas (99.995% purity) in six nines hydrogen¹ was used for substrate etching.

Substrates.—Experiments were carried out on molybdenum substrates. These substrates, of 99.95% purity, were obtained in 10 mil thick, rolled strips,⁴ and were cut into $\frac{1}{2} \times \frac{1}{2}$ in. squares for use in this work.

Procedure.—Adhesion of the polycrystalline layers, as well as their morphology, is dependent on the manner in which substrates are prepared. Mechanical polishing was used for initial experiments, and con-

 ¹ Matheson Gas Products, East Rutherford, New Jersey 07073.
 ² Alfa Products Division, Beverly, Massachusetts 01915.
 ³ Precision Gas Products, Inc., Rahway, New Jersey 07065.
 ⁴ Materials Research Corporation, Orangeburg, New York.

sisted of successive lapping and ultrasonic cleaning, down to a final lap with 0.6 μ m diamond paste. Optically flat substrates were obtained in this manner.

We have investigated the possibility of avoiding this tedious process by direct chemical etching, using a mixture of H_2O_2 , NH_4OH , and H_2O in a 2:1:7 ratio by volume. This etch provides a removal rate of 3.2 μ m/min at 75°C, and leaves no residual stain on the substrates. Typically, 3-5 μ m of molybdenum was etched off in order to expose a clean working surface. Upon etching, substrates were stored in methanol and blown dry in filtered nitrogen before further use.

A series of experiments were conducted using both mechanically polished and chemically etched substrates to determine if there was any difference in the quality of the gallium arsenide layers. Furthermore, both chemical vapor deposition and conventional vacuum evaporation were used to form the germanium layers on these substrates.

The procedure for growth on CVD germanium layers was as follows: Substrates were transferred to the reactor and placed on the susceptor such that they were nearly perpendicular to the direction of gas flow. The system was evacuated with a mechanical pump before establishing a flow of hydrogen (2.5 l/min). The susceptor was then heated to 1000°C and maintained at this temperature for 15 min. This was followed by the introduction of HCl gas at a flow rate⁵ of 1.5 ml/min, for a 5 min *in situ* etch.

The germanium layer was next grown on this substrate after lowering the substrate temperature to 900°C. This was done by introducing germane at a flow rate of 1.0 ml/min. A typical growth rate of 0.6 μ m/min was observed for these conditions. A short 15 min anneal treatment, at 900°C, was provided after shutting off the germane supply. Next, the reactor temperature was lowered to that required to grow the gallium arsenide (600°-750°C in our experiments), and the hydrogen flow raised to 5 l/min. At this point an arsine flow of 15 ml/min was established. The subsequent GaAs layer was grown by introducing trimethylgallium (TMG) by means of hydrogen flow through the bubbler at rates up to 10 ml/min.

In situations where evaporated germanium layers were used, the cleaned substrate was given the $H_2/$ HCl treatments at 1000°C before transfer to the vacuum evaporator. Upon germanium deposition, the substrate was returned to the reactor where it was given a 15 min anneal in hydrogen gas, at 900°C, prior to the introduction of arsine and the subsequent growth of gallium arsenide.

Film thicknesses were determined by weighing the substrates before and after growth, using a Mettler Model H51 microbalance, and using specific gravity values for single crystal germanium and gallium arsenide (5.3267 and 5.323, respectively). All of the CVD growth, etch, and anneal steps were performed in a single reactor operation. The cold wall system has low thermal mass so that shifts to the appropriate operating temperature for each step could be made very rapidly, as required.

Results

As expected, evaporated germanium layers on polished substrates were specular in character, whereas those on the etched substrates were diffuse, with a frosted appearance. The morphology of GaAs layers on both evaporated and CVD germanium, however, was nearly identical. Somewhat larger crystal sizes were obtained with CVD germanium layers than with evaporated layers.

Figure 1 shows comparison scanning electron microscope (SEM) photographs of GaAs layers grown on CVD germanium, with both polished and etched sub-

 5 In this paper, flow rates for HCl, GeH₄, and AsH₃ are all quoted in terms of the actual reactant content of the diluted gas.



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Fig. 1. Morphology of GaAs layers on CVD Ge: (a) polished molybdenum substrate; (b) etched molybdenum substrate.

strates. These layers are almost identical in appearance, and clearly establish the usefulness of the chemical etching process. Very similar results were obtained for layers grown on evaporated germanium.

Figure 2 shows an SEM photograph of a 5 μ m thick gallium arsenide layer, grown on a 1 μ m thick CVD germanium layer, with a chemically etched molybdenum substrate. Crystallite size is in the 5-15 μ m range for gallium arsenide layers of these thicknesses. It is expected that crystal size will improve by increasing film thickness, however, economic considerations preclude the use of thicker films for low cost solar cell applications.

The electronic properties of polycrystalline films on metallic substrates are difficult to determine and harder to evaluate. Consequently, we have placed our emphasis on studying the electrical characteristics of devices made from these films. All gallium arsenide layers, as grown, were first subjected to a simple tungsten probe with a V-I curve tracer. Results are not useful in the forward direction because of the extremely large spreading resistance, as well as the sensitivity to probe pressure. The reverse bias breakdown voltage, however, is a useful indicator of device quality. Typically, breakdown voltages of 10V and higher are considered useful if they are observed over the entire cell area. Voltages as low as 1 and as high as 35V have been measured in some layers. In a



Fig. 2. Morphology of 5 μ m GaAs layer on 1 μ m CVD Ge (etched molybdenum substrate).

few situations, layer conversion to p-type has also been observed.

Gold-gallium arsenide Schottky diodes have been made on these GaAs substrates. Figure 3 shows the V-I characteristics⁶ for one such device, (dot area 0.002 cm²). Here, the diode "knee" is at 0.6V. The device shows a series resistance of 12.5 Ω , primarily due to the contacts, rather than to the bulk resistivity of the gallium arsenide. Breakdown occurs at 30V in this device, however, considerable softness in the reverse characteristic is noted by 15V. Figure 4 shows the $1/C^2$ vs. V plot for this diode, indicating a carrier concentration of 7 - 13 \times 10¹⁵/cm³ for these layers.

Discussion

Devices were made on substrates cut from rolled molybdenum strip material. Work damage in this material probably extends throughout its entire thickness; consequently, the chemical treatment serves purely to clean up the surface and remove surface features such as scratches prior to introduction into the reactor.

The 1000°C treatment in hydrogen gas does not result in any annealing of the substrates since an anneal temperature of 2000°C is more appropriate for molybdenum. In addition, experiments with the HCl gas etch step indicate no measurable removal of material. Nevertheless, we have consistently observed that layers formed after these treatments have better morphology and also show firmer adhesion to the molybdenum substrate. It is probable that this process removes the fresh oxide which typically forms, to a few angstroms thickness, on surfaces which are chemically treated. It is also possible that these steps activate the substrate surface and so assist in the nucleation process.

Germanium belongs to group IV of the periodic table, and can behave as either p or n-type. depending on the manner in which it is incorporated into the GaAs lattice. At high temperatures, such as those encountered during GaAs growth by chemical vapor deposition, strong n-type doping is commonly encountered. Thus, the interdiffusion of germanium into the gallium arsenide results in an n^+ -GaAs interface.



Fig. 3. V-I characteristics for Au-Schottky diode: (a) low level, 0.2 V/DIV, 0.1 mA/DIV; (b) extended voltage range, 5 V/DIV, 0.5 mA/DIV; (c) extended current range, 0.5 V/DIV, 20 mA/DIV.

Note, however, that the germanium layer itself is arsenic doped so that it is n^+ -type. As a consequence, the over-all structure consists of $n-n^+$ GaAs, n^+ -Ge, and a molybdenum substrate.

Growth of the germanium layer is accomplished at 900° C, *i.e.*, within 36° of its melting point. We estimate a factor of three improvement in the grain size over that obtained by growth at a more conventional temperature (*e.g.*, 700°C). In part, this improvement is

^e Comparable characteristics have been observed for devices on both evaporated and CVD germanium layers.



BIAS VOLTAGE (V)

Fig. 4. C-V characteristic, indicating effective carrier concentration.

due to the rapid movement of grain boundary vacancies which leads to the coalescence of crystallites at this temperature.

Problems encountered during the growth of GaAs on Ge layers are illustrated by the phase diagram of the Ga-Ge-As system (7), shown in Fig. 5. We note that germanium is not miscible in gallium arsenide; however, one compound (GeAs), two binary eutectics, and one ternary peritectic are all possible during the formation of these layers. Indeed, many problems are due to the formation of one or more of these. One such problem is evidenced by what would appear to be massive autodoping of the gallium arsenide layer by germanium. In some cases, energy dispersive spectroscopy (EDS) data have shown the presence of germanium, arsenic, and gallium over the entire surface layer. This problem is largely caused by the presence of high concentrations of gallium in GeAs, together with the primary GaAs phase, and has been eliminated by growth at reduced temperatures. This also greatly reduces the possibility of the ternary peritectic formation which can result in clumps in the film.



Fig. 5. The Ge-Ga-As system [Ref. (7)]



Fig. 6. Whisker formation

A second problem we have noted is that of whisker growth, as shown in the SEM photographs of Fig. 6. EDS data show the presence of germanium, arsenic, and gallium in this whisker as well as on the surface of the grown layer. This problem comes about for the following reasons. The TMG-AsH₃ reaction is (8) a heterogeneous one, and comes about by the adsorption of both reagents on the surface, followed by a surface reaction (Langmuir-Hinshelwood mechanism). From thermodynamics and kinetic considerations it has been shown (9) that there is a critical partial pressure for the TMG at any given growth temperature. When exceeded, this results in the formation of a liquid gallium phase which can be transported to the substrate surface by diffusion through the stagnant layer. The amount of liquid gallium delivered to the germanium surface falls as the growth temperature is increased, or as the TMG/AsH_3 mole ratio is reduced. Thus, whisker growth, as well as the presence of gallium on the surface, can be eliminated by sufficiently reducing the mole ratio and/or by raising the growth temperature. Unfortunately, growth at elevated temperatures is not desirable, because of alloy and compound formation, as mentioned earlier. Consequently, we have reduced the mole ratio of TMG/AsH₃ to 1/16 in order to obtain whisker-free growth at temperatures as low as 600°C.

We have noted that the proper sequencing of the arrival of arsenic and gallium reactants into the growth chamber plays an important role in determining the quality of the gallium arsenide layer. This is due to the fact that the surface of the germanium layer is exposed to both arsenic and gallium during the initial growth of GaAs. Consequently, the formation of Ge/As alloys or compounds can occur at this time. Additionally, gallium is known to have a high solubility in these Ge/As phases, so that this material can penetrate through the entire subsequent layer of GaAs. This effect can be particularly severe in polycrystalline film growth where its movement along grain boundaries can be very rapid. We can expect, therefore, that two GaAs layers, grown under otherwise identical conditions, can result in different morphology as well as chemical content. Figure 7a shows x-ray diffraction data⁷ taken on sample A where the time between arrival of the arsenic and the gallium is short. This shows only peaks for the different orientations of gal-

⁷ Only part of the run is shown here for ease of data presentation. Specifically, the region showing the primary (111) peak has been omitted. The 220 and 311 peaks are located at $2\theta = 45.4^{\circ}$ and 53.8°, respectively.



Fig. 7. X-ray diffraction data for polycrystalline GaAs on CVD-Ge: (a) sample A; (b) sample B.

lium arsenide, however, as seen in Fig. 7b (sample B), many additional peaks appear when this time is increased. Some have been identified as mixtures and compounds of germanium, arsenic, and gallium.

As seen from the above, the epitaxial growth of high quality layers of polycrystalline GaAs on Ge is at best a difficult task. Many workers have noted the difficulty of fabricating device quality layers on single crystal substrates, although the problem appears to be a deceptively simple one due to the near perfect match of the GaAs and Ge crystal lattices. We note here that growth of polycrystalline layers has the added problem that solutions of Ga in Ge/As alloys transport readily throughout the GaAs layer by movement along grain boundaries. Nevertheless, the growth of high quality layers of polycrystalline GaAs on Ge can be achieved by careful attention to the details outlined above.

Finally, we note some uncertainty in interpreting the C-V data of Fig. 4. In our system, films of GaAs grown on single crystalline GaAs substrates typically fall in the 2-5 \times 10¹⁵/cm³ carrier concentration range for the growth parameters given here. In Fig. 4, however, the slope of the C-V characteristic indicates a carrier concentration of 1.3 imes 10¹⁶/cm³ at low bias. At larger reverse voltages, however, the slope of this curve increases. This is not due to the presence of traps in the layer, which typically show up as a fall in this slope. Rather, it is probably due to the uncovering of bound charges at the grain boundary surface as the depletion layer expands with increasing reverse voltage.

Conclusions

We have shown that the epitaxial growth of gallium arsenide on germanium involves careful attention to compromise with the process parameters. Furthermore, device quality layers are more difficult to achieve with polycrystalline films because of the tendency for gallium-based solutions to move rapidly along grain boundaries during film growth. Layers with an effective electron concentration of (7-13) \times 10¹⁵/cm³ have been demonstrated for the first time, as have Schottky diodes with breakdown voltages in excess of 30V.

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