N94-11405

# INVESTIGATION OF ZnSe-COATED SILICON SUBSTRATES FOR GaAs SOLAR CELLS[1]

Daniel A. Huber, Larry C. Olsen, Glen Dunham, and F. William Addis

Washington State University / Tri-Cities
100 Sprout Road
Richland, WA 99352

Studies are being carried out to determine the feasibility of using ZnSe as a buffer layer for GaAs solar cells grown on silicon. This study was motivated by reports in the literature indicating ZnSe films had been grown by MOCVD onto silicon with EPD values of $2x10^5$ $cm^{-2}$, even though the lattice mismatch between silicon and ZnSe is 4.16 %. These results combined with the fact that ZnSe and GaAs are lattice matched to within 0.24 % suggest that the prospects for growing high efficiency GaAs solar cells onto ZnSe-coated silicon are very good. Work to date has emphasized development of procedures for MOCVD growth of (100) ZnSe onto (100) silicon wafers, and subsequent growth of GaAs films on ZnSe/Si substrates. In order to grow high quality single crystal GaAs with a (100) orientation, which is desirable for solar cells, one must grow single crystal (100) ZnSe onto silicon substrates. A process for growth of (100) ZnSe has been developed involving a two-step growth procedure at 450°C. Single crystal, (100) GaAs films have been grown onto the (100) ZnSe/Si substrates at 610°C that are adherent and specular. Minority carrier diffusion lengths for the GaAs films grown on ZnSe/Si substrates have been determined from photoresponse properties of Al/GaAs Schottky barriers. Diffusion lengths for n-type GaAs films are currently on the order of 0.3 μm compared to 2.0 μm for GaAs films grown simultaneously by homoepitaxy.

## INTRODUCTION

This paper concerns investigations of ZnSe as a buffer layer for Single crystal GaAs solar cells grown on silicon. Single crystal silicon is considered a low cost substrate for GaAs solar cells. Since silicon has a lower density than GaAs and can be thinned to less than 2 mils, GaAs cells grown on silicon could lead to high efficiency cells at reduced cost and weight. Significant progress has been made regarding the growth of efficient GaAs cells directly on silicon. However, investigations of GaAs cells on single crystal silicon have not resulted in the high efficiencies that are possible with GaAs substrates. The major problem that must be overcome is related to the high dislocation or other defect density in the GaAs. Although Si has a diamond structure and GaAs a zinc-blende crystal structure, their lattice constants differ

[1]This work is funded by the Space Power Division, Phillips Laboratory, Kirtland Air Force Base.

by 4%. As a result, when GaAs films are grown on silicon, the films are characterized by large defect densities. In particular, if a simple two-step growth technique is carried out, dislocation densities > $10^8$ $cm^{-2}$ are observed for GaAs films grown directly on silicon. Using a thermal-cycle-growth (TCG) process , the dislocation density in GaAs films grown on silicon has been reduced below $10^7$ $cm^{-2}$, which allowed the fabrication of GaAs cells (on silicon) with an AM1.5 efficiency of 18% (ref. 1). Other researchers have utilized a strained layer superlattice (SLS) to reduce dislocation densities. These procedures are relatively complicated and produce only marginal decreases in defect density over thermal-cycle-growth.

The potential use of a strain relieving ZnSe buffer layer to reduce the dislocation density in GaAs films grown on silicon presents the possibility of a much simpler process for growth of high efficiency GaAs cells on silicon. Figure 1 describes the basic approach to cell design using a ZnSe buffer. There is experimental evidence that deposited crystalline films of ZnSe provide strain relief both in the ZnSe film itself and in crystalline films grown on a ZnSe film. Mino, et al., observed that ZnSe films grown by MBE on silicon substrates were characterized by an EPD density of $3x10^5$ $cm^{-2}$ (ref. 2). Lee, et al., have grown GaAs films on silicon substrates with ZnSe buffer layers that were characterized by an EPD count of $2 \times 10^5$ $cm^{-2}$ (ref. 3). Additionally, Lee, et. al., have grown InP films on ZnSe-coated silicon that exhibited a PL spectrum very similar to that measured for InP films grown on InP substrates (ref. 4). Whereas ZnSe and GaAs are lattice matched to within 0.24%, ZnSe and InP are lattice mismatched by 3.4%, and silicon and InP are lattice mismatched by 7.46%. Thus, there is clearly evidence that ZnSe can act as an effective buffer layer between lattice mismatched systems. It appears that the weaker bond strength in ZnSe relative to Si and the III-V compounds allows the ZnSe layer to provide strain relief, which can lead to the misfit dislocations being produced in the ZnSe layer. Table 1 gives some properties of, Si, GaAs and ZnSe. Note that ZnSe is a much softer material than Si and GaAs as evidenced by the Knoop hardness value. Thus, one may consider the softness of ZnSe as the reason for it being an effective buffer layer.

Investigations reported here are in the early stages of the planned effort. To date, studies have focused on the development of MOCVD growth of ZnSe on silicon, and MOCVD growth of GaAs films on ZnSe-coated silicon. Solar cell studies have just recently begun. Discussions of results in these areas follow. Ultimately, the objective of this work is to grow a GaAs cell structure as described in Figure 2. The ZnSe buffer layer would be doped n-type and since the electron affinity is essentially the same as that for silicon and GaAs there should be no significant resistance at the n-GaAs/n-ZnSe and n-ZnSe/n-Si interfaces.

## MOCVD GROWTH OF ZnSe ON SILICON

ZnSe is grown by MOCVD in a SPIRE 500XT reactor by reacting a zinc adduct and $H_2Se$. The zinc adduct was formed by reacting dimethylzinc (DMZn) and triethylamine (TEN). The adduct (DMZn/TEN) source provides a large molecule with zinc at the center and does not react so readily with $H_2Se$. The use of the adduct has allowed MOCVD growth of ZnSe with minimal prereaction. The optimum substrate temperature for growth of ZnSe on silicon appears to be in the range of 400°C to 450°C. Although some effort has been devoted to investigating approaches to MOCVD growth of conductive ZnSe, the primary focus has been placed on determining a procedure for growing (100) oriented ZnSe on (100) Si, and the deposition of (100) GaAs on (100) oriented ZnSe/Si substrates. We have found that Al, In and iodine will dope ZnSe n-type. The exact approach to be use for doping ZnSe will be determined after processes for growing the complete solar cell structure are selected.

MOCVD growth of ZnSe at 400°C to 450°C on (100) silicon at a single deposition rate will typically lead to either polycrystalline or crystalline films with a preferred (111) orientation. Growth of GaAs on such ZnSe films would yield low quality GaAs for solar cell fabrication. In order to grow single crystal (100) GaAs, it is necessary that the ZnSe film on the ZnSe/Si substrate have a (100) orientation. One growth procedure that yields (100) ZnSe films on (100) silicon involves a two-step process, namely, nucleation and growth steps. The nucleation step involves MOCVD growth of a few hundred angstroms of ZnSe at 1 Å/s, followed by growth of the remainder of the film at a rate of 5-10 Å/sec. Results of XRD analyses for a ZnSe film grown with a single rate and for a film grown with a two-step procedure are given in Figures 3 and 4, respectively. Figure 3A shows XRD results for polycrystalline ZnSe film with a strong (111) orientation, and Figure 3B shows results for a GaAs film grown on this ZnSe film. The GaAs film was clearly of poor quality. Figure 4A gives results for a single crystal (100) ZnSe film grown with a two-step procedure, while Figure 4B shows the improved quality from the XRD spectrum for a growth relative after growing GaAs at 620°C.

Additional studies are required in order to optimize the growth process for ZnSe on silicon. Two aspects are being pursued, namely, optimization of the process with respect to the impact on the properties of GaAs films grown on ZnSe/Si substrates and identification of procedures compatible with doping the ZnSe film.

## MOCVD GROWTH OF GaAs ON ZnSe/Si SUBSTRATES

Once procedures were developed for growth of (100) ZnSe on silicon, progress was made in the growth of GaAs on ZnSe/Si substrates. Initially, polycrystalline GaAs films were grown because the ZnSe films were polycrystalline. The two-step process in growing ZnSe allowed the growth of single crystal (100) GaAs films. Scanning electron micrographs of three GaAs films are shown in Figure 5A, 5B and 5C. Figure 5A shows a polycrystalline GaAs film grown on a ZnSe/Si substrate for which the ZnSe was grown at 450°C with a one-step process. Figure 5B shows a SEM of sample 92GZS165, a structure consisting of GaAs grown on a ZnSe/Si substrate for which the ZnSe film was grown with a two-step process. Although the GaAs film on sample 92GZS165 is single crystal, it is very defective. An improvement in the GaAs film was achieved in the case of sample 92GZS190 which is described by Figure 5C. Note that the magnification is 5 kX for these micrographs. In this case, the ZnSe film was capped with a thin GaAs layer before removing it from the MOCVD system. Refinement of these processes is underway. As illustrated by these scanning electron micrographs, however, improvement in GaAs film quality has been accomplished. As discussed in a subsequent section improvements in minority carrier diffusion length are also occurring.

In addition to examination by a scanning electron microscope, TEM studies and charged ion concentration profiles taken with a electrochemical C-V profiler are being done for physical characterization. TEM studies are underway and will be reported at a later date. Electrochemical C-V profiles (Polaron profiles) are shown for two n-type GaAs films in Figure 6A and 6B. The profile for sample 92GZS190 (Figure 6A) shows a high charged ion density at a depth ≥1 μm. We interpret these results as indicating there is a large density of defects that are charged and can be detected by the C-V measurement. Figure 6B shows a profile for sample 92GZS204, a GaAs film grown on a ZnSe/Si substrate for which the ZnSe film growth process had been further optimized.

Single crystal GaAs films have been grown on ZnSe on GaAs substrates for comparison. This system is pertinent since the same concerns exist for nucleation of high-quality GaAs on ZnSe but without the strain caused by the silicon substrate. Figure 6C shows the electrochemical C-V profile for sample 92GZG262, a GaAs film grown on a ZnSe/GaAs substrate. Absent is the high charge concentration found in samples grown on silicon substrates. This indicates that the increasing charge density in the samples on ZnSe/Si may be due to a large density of defects rather than interdiffusion. It is reasonable to assume that the large defect density in the films grown on silicon substrates could provide "pipelines" for diffusion transport from the ZnSe. A small increase in charged impurity concentration occurs in sample 92GZG262 close to the GaAs/ZnSe interface. It is not clear whether this indicates interdiffusion or an artifact of the C-V measurement at the heterojunction.

## MINORITY CARRIER PROPERTIES

Minority carrier diffusion lengths of GaAs films have been measured by analyzing the photoresponse of Al/n-GaAs Schottky barriers as depicted in Figure 7. We have found that Al will consistently form a Schottky barrier on n-type GaAs if the Al is vacuum deposited at a relatively fast rate, say ≥ than 15 Å/s, at pressures around $2\times10^{-6}$. Al thicknesses between 80 and 100 Å are utilized so that the aluminum layer is thin enough to pass a significant fraction of an incident flux of photons into the GaAs region. If photons of energy $h\nu \geq E_g$ are incident on a sample and each photon creates one electron-hole pair, the maximum possible photocurrent density is given by:

$$J_{max} = q \cdot F \tag{1}$$

where F is the incident photon flux. The two major contributions to the photocurrent of the Schottky barrier are due to current collected from the depletion region and from the bulk. The photocurrent can be written as:

$$J_{ph} = J(\text{Depletion Region}) + J(\text{Bulk}) \tag{2}$$

where

$$J(\text{Depletion Region}) = q\,T\,F\,f\,[1-\exp(-\alpha W)] \quad (3)$$

and

$$J(\text{Bulk}) = qTF\exp(-\alpha W)\,[\,\alpha L/(1+\alpha L)\,] \quad (4)$$

where T is the transmittance of photons through the metal film, F is the incident photon flux at a specific wavelength of light, f is a collection factor for the depletion region, $\alpha$ is the absorption coefficient, W is the depletion region width, and L is the minority carrier diffusion length. We have introduced a "collection factor" for the depletion region. Thus, although a high field may exist in this region, we assume that the probability of a carrier being swept out of the region may be less than 1.0. Such an assumption allows one to fit data for defective material. It is being assumed, however, that carriers diffusing from the bulk have sufficient velocity to escape with a probability of 1.0. This model is clearly a simplification of a rather complex problem, but provides an approach for evaluating material. As the material improves in quality, the "f" factor should approach 1.0 and diffusion lengths should increase in value. In high-quality material one must also account for the bending of the bands near the metal-semiconductor interface by an image force. The band bending occurs over 50 Å and thus decreases the response to UV light. Finally, it should be noted that the reflection of light from the metal surface and adsorption in the metal film are accounted for in T.

The collection of current from the bulk of the Schottky barrier device is essentially the same as from the base of a p-n junction device with a modification due to the transmittance being less than 100%. Collection of carriers from the bulk is dependent upon the minority carriers having sufficient lifetime (diffusion length) to diffuse to the depletion region. The above expression for J(Bulk) is based on the assumption that the back contact (contact other than the Schottky barrier) is ohmic and that the device thickness is much greater than the minority carrier diffusion length.

We define the external photoresponse of a Schottky barrier by the relationship

$$J_{ph} = Q_{ext} \cdot J_{max} \quad (5)$$

From the above results, we have

$$Q_{ext} = T \cdot \{\, f\,[1-\exp(-\alpha W)\,] + \exp(\alpha W) \cdot [\,\alpha L/(1+\alpha L)\,]\,\} \quad (6)$$

The internal photoresponse ($Q_{int}$) is given by $Q_{ext}/T$. $Q_{int}$ is independent of the film transmittance, and thus only depends on the GaAs film properties. To determine the internal photoresponse, the transmittance $T(\lambda)$ must be obtained for the wavelength range of interest.

Calculation of the transmittance T requires knowledge of the optical constants n and k of the Al film. The optical properties of thin aluminum films can vary greatly with deposition conditions. The optical constants are determined from measured values of transmittance (T) and reflectance (R) for Al films deposited on quartz witnesses. The optical constants, n and k, of Al films are calculated with a computer-aided analysis that utilizes values of T and R for each photon wavelength and the optical constants of the quartz substrate. Figure 8 demonstrates the results of modeling the reflection and transmission from an Al Schottky barrier film on GaAs. After determining the optical properties of the Al film and measuring the photoresponse and reflectance of the Schottky barrier device, a data file is constructed that contained the n and k values of the Al film at each photon wavelength, the n and k values from literature of the GaAs at each photon wavelength, the GaAs layer thickness, the depletion width, and assumed values for f and L. Values of the two fitting parameters, collection factor f and diffusion length, are then varied until the best fit to $Q_{ext}$ is attained.

Figure 9 shows results for n-type GaAs films grown on ZnSe/Si substrates. Table 2 summarizes results of photoresponse analysis. Analysis of data for a n-type GaAs film grown simultaneously on GaAs indicates a diffusion length of 2.0 μm, and establishes a reference value with which to compare results obtained for films grown on ZnSe/Si substrates. As the quality of the GaAs films has improved, the internal photoresponse has improved, which is interpreted in terms of an increasing minority carrier diffusion length.

## CONCLUSIONS

The objective of these studies is to determine the feasibility of ZnSe buffer layers for growth of GaAs solar cells on silicon substrates. Work to date has primarily involved the development of procedures for MOCVD growth of (100) ZnSe on (100) silicon, and growth of GaAs films on ZnSe/Si substrates. Progress has been made in both areas. A process for growth of single crystal (100) ZnSe on (100) silicon at 450°C has been developed. Films are very specular and uniform. Single crystal GaAs films with (100) orientation have been grown at 620 °C that exhibit finite minority carrier diffusion lengths. Specifically, n-type GaAs films have been grown that have minority carrier diffusion lengths of approximately 0.3 μm. N-type GaAs films grown on GaAs substrates at 620°C were characterized as having a diffusion length of 2 μm. It is expected that improved understanding of film nucleation at the Si-ZnSe and ZnSe-GaAs interfaces will lead to growth of n-type GaAs films with diffusion lengths greater than 1.0 μm and p-type films with diffusion lengths significantly greater than 1.0 μm. Such results would allow the fabrication of high efficiency GaAs cells on ZnSe/Si substrates.

## REFERENCES


[1] S. M. Vernon, et al., "Efficiency Improvements in GaAs on Si Solar Cells," 20th IEEE Photovoltaic Specialists Conference (1988), p. 481.

[2] Naoki Mino, et al., "Epitaxial Growth of High Quality ZnSe on Si Substrates by Molecular Beam Epitaxy and Application to dc Electroluminescent Cells," Journal of Applied Physics 58, 793 (1985).

[3] M. K. Lee et. al., "Improvements in the heteroepitaxy of GaAs on Si by incorporating a ZnSe buffer layer," Applied Physics Letters 59, 207 (1991).

[4] M. K. Lee, et al., "Growth and Characterization of InP Epilayers on ZnSe-Coated Si Substrates by Low-Pressure Metalorganic Chemical Vapor Deposition," Applied Physics Letters 53, 107 (1988).


Table 1. Material Parameters for Si, GaAs and ZnSe

| Material | Si | GaAs | ZnSe |
|---|---|---|---|
| Lattice Constant (Å) | 5.43095 | 5.6534 | 5.6686 |
| Coefficient of Expansion (°C$^{-1}$) | 2.32 x $10^{-6}$ | 5.75 x $10^{-6}$ | 7.0 x $10^{-6}$ |
| Bandgap(eV) | 1.12 | 1.42 | 2.67 |
| Electron Affinity (eV) | 4.05 | 4.07 | 4.09 |
| Crystal Structure | Diamond Cubic | Zinc-blend | Zinc-blend |
| Density (g/cm$^2$) | 2.33 | 5.32 | 5.32 |
| Knoop Hardness | 1150 | 780 | 150 |

Table 2. Minority Carrier Properties Of GaAs Films Grown On ZnSe/Si Substrates

| Device | Depletion Width (μm) | Collection Factor | Carrier Concentration (cm$^{-3}$) | Diffusion Length (μm) |
|---|---|---|---|---|
| 92GZS171 | 0.05 | 0.02 | 1 x $10^{17}$ | 0.1 |
| 92GZS190 | 0.05 | 0.30 | 1 x $10^{17}$ | 0.1 |
| 92GZS204 | 0.10 | 0.75 | 2 x $10^{17}$ | 0.3 |
| 92GG825 | 0.10 | 1.00 | 4 x $10^{17}$ | 2.0 |

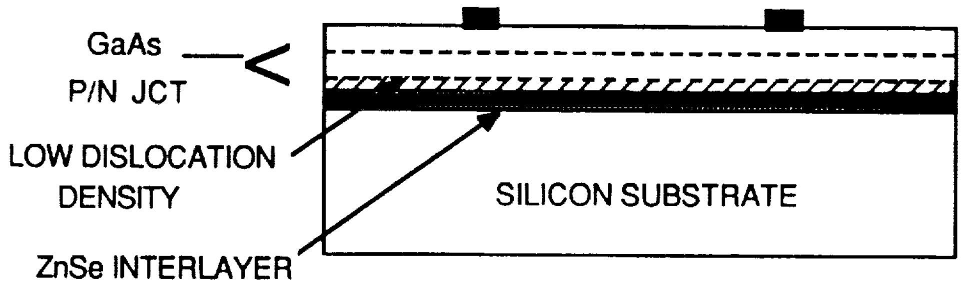


Figure 1. Approach to fabrication of GaAs solar cells being investigated in these studies. ZnSe layer provides strain relief and allows formation of dislocations near interfaces so that propagation of threading dislocations into GaAs is minimized.

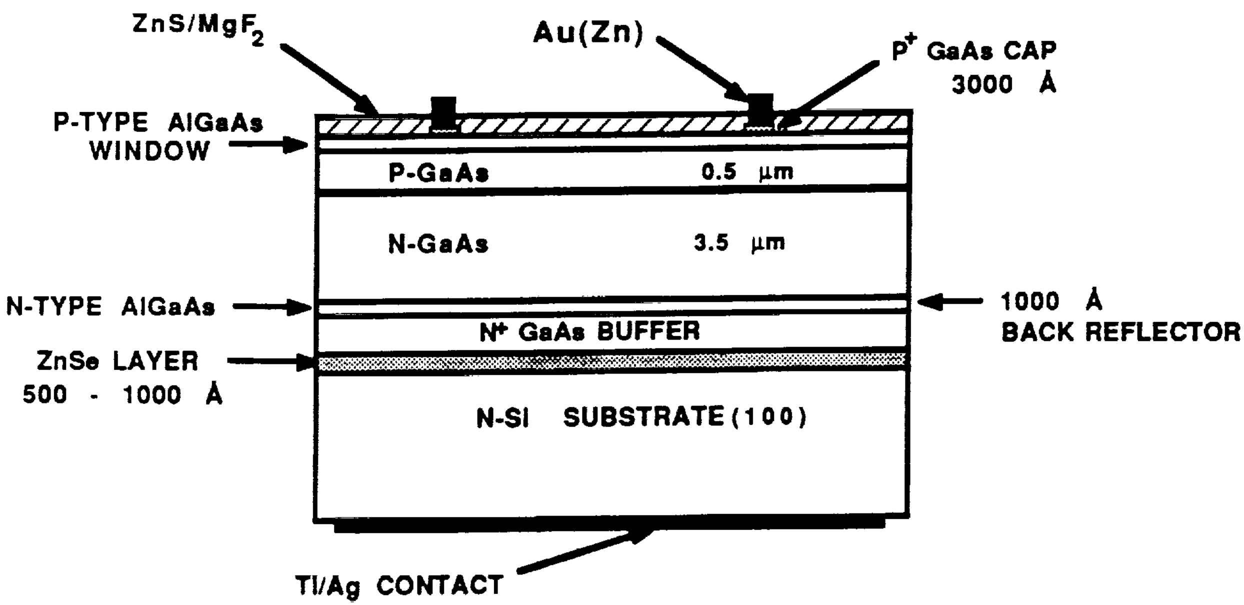


Figure 2. Planned structure of P/N GaAs Solar Cell onto a ZnSe-Coated Silicon Substrate.

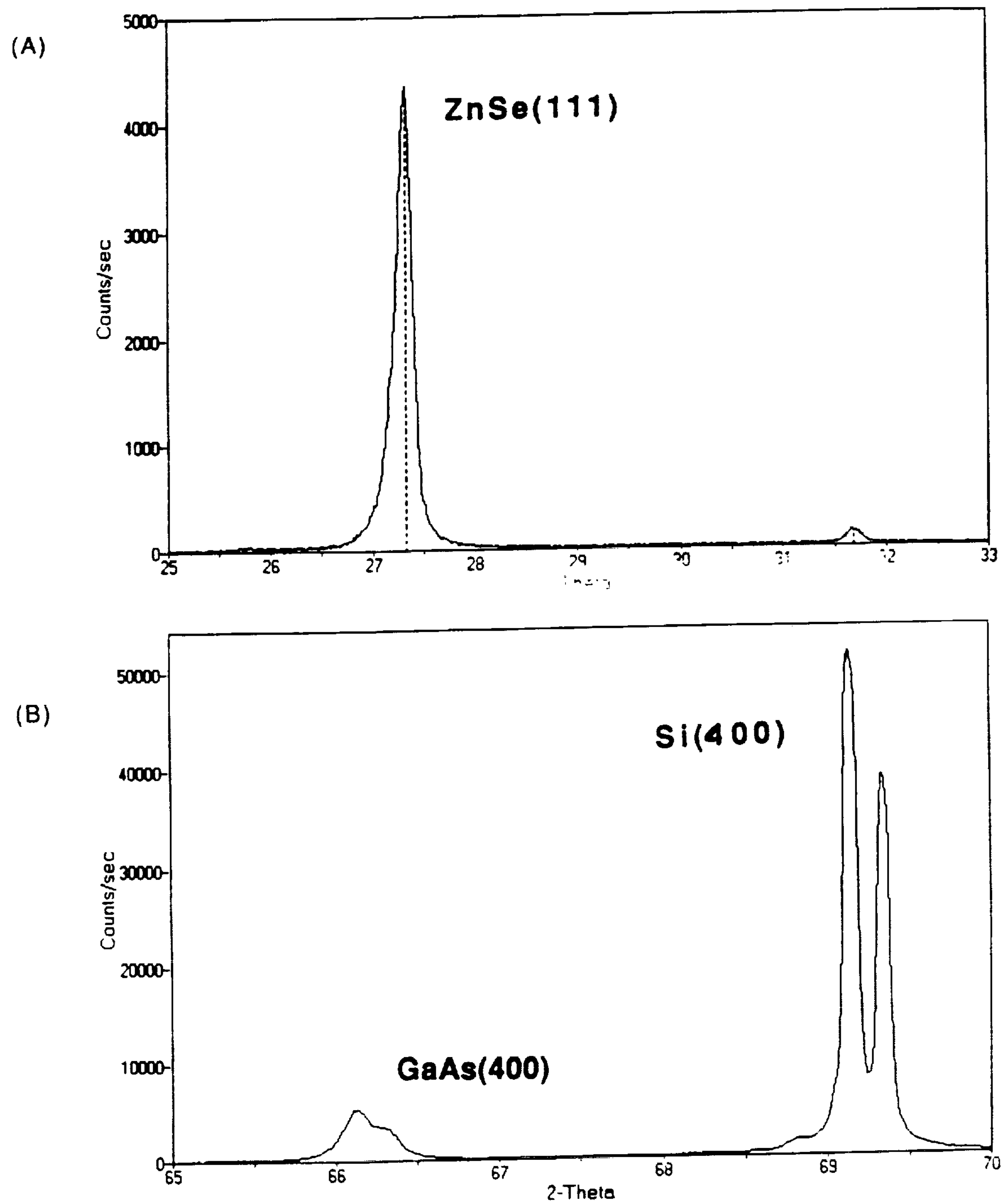


Figure 3. (A) XRD Spectrum for 92ZS070 Showing the Strong (111) Diffraction Peak; (B) XRD Spectrum for the GaAs Film Grown on 92ZS070 (Giving Sample 92GZS070).

(A)

(B)

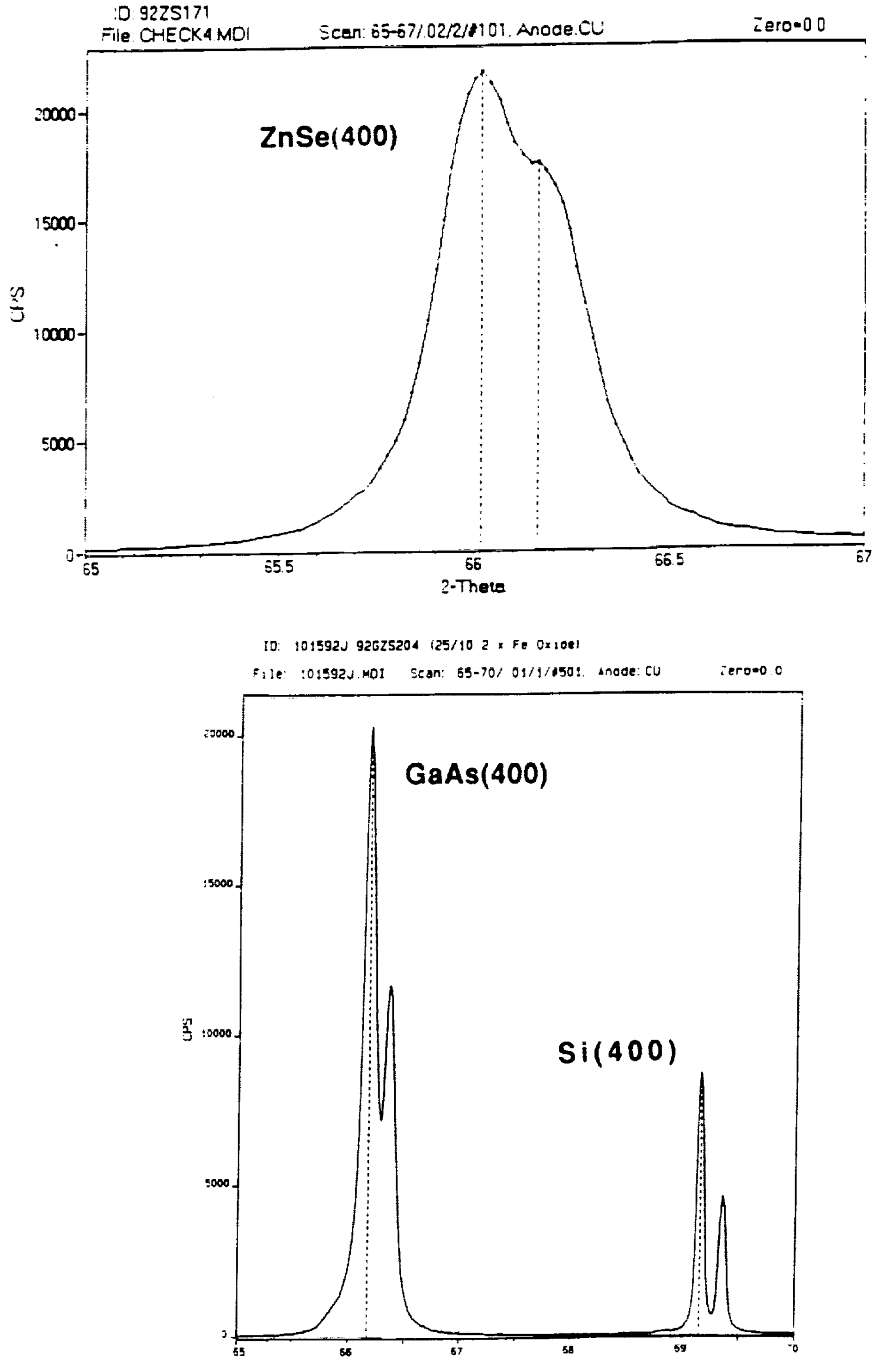


Figure 4 (A) XRD Spectrum for 92ZS171 Showing the ZnSe (400) Reflection with $K_{\alpha}1$, $K_{\alpha}2$ Peaks Just Resolved. Only (100) Type Peaks Were Observed. (B) XRD Spectrum for Sample 92GZS204 with Single Crystal GaAs Film Grown On ZnSe/Si Substrate.

(A)

(B)

(C)

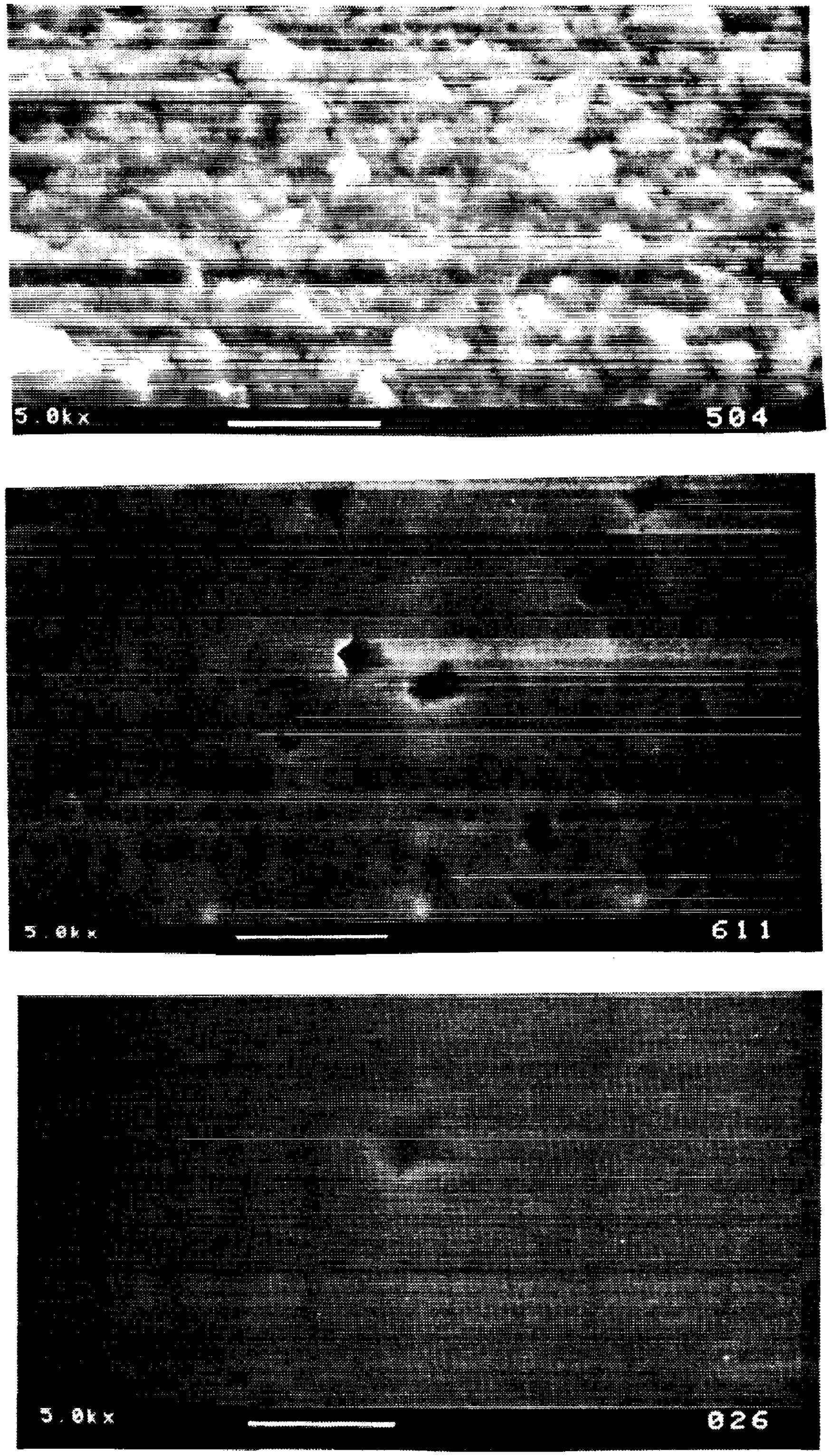


Figure 5. Scanning Electron Micrographs for Three GaAs Films Grown on ZnSe/Si Substrates: (A) Sample 92GZS094, a GaAs Film Grown On ZnSe/Si with the ZnSe Having (111) Orientation; (B) Sample 92GZS165, a GaAs Film Grown on (100) ZnSe/Si (see text) ; (C) Sample 92GZS190, a GaAs Film Grown on (100) ZnSe/Si and an Improved Process (see text).

(A)

(B)

(C)

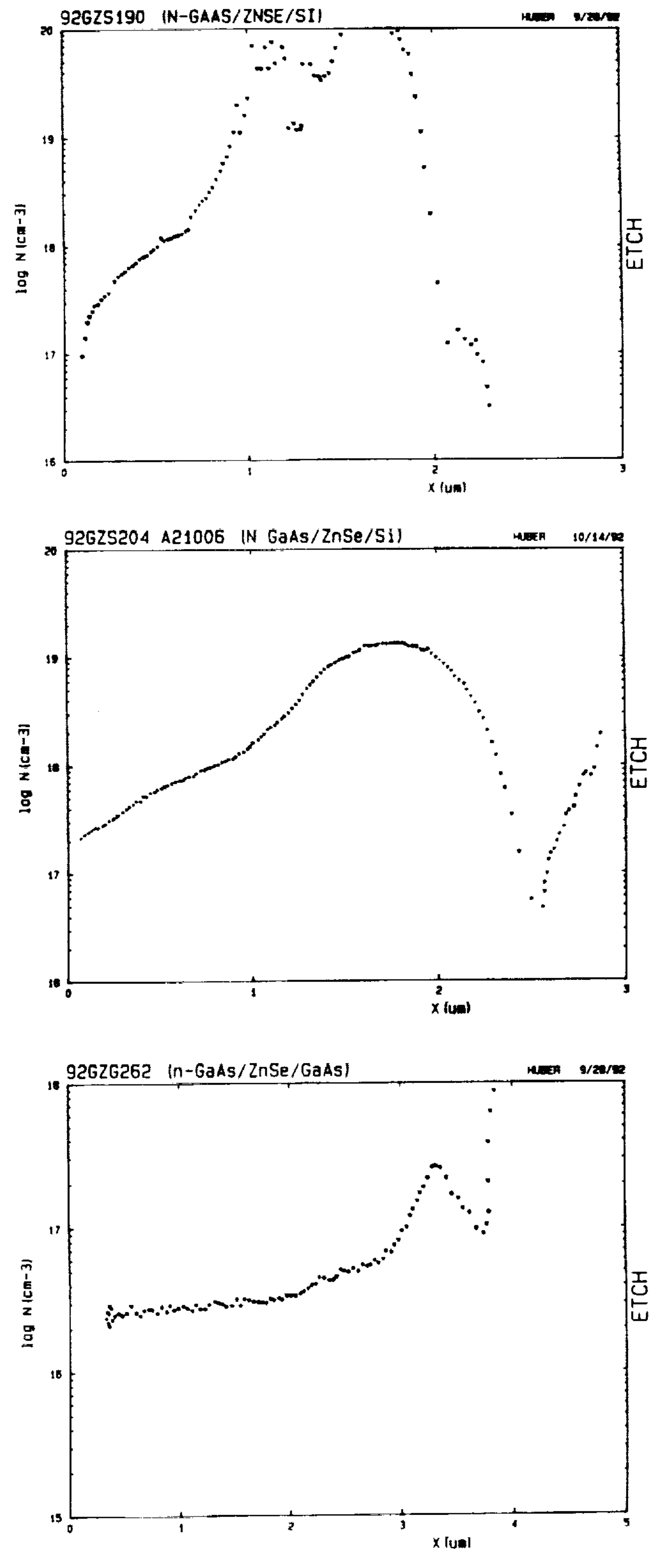


Figure 6. Charged Impurity Concentration Profiles Acquired for; (A) Sample 92GZS190; (B) Sample 92GZS204; (C) Sample 92GZG262.

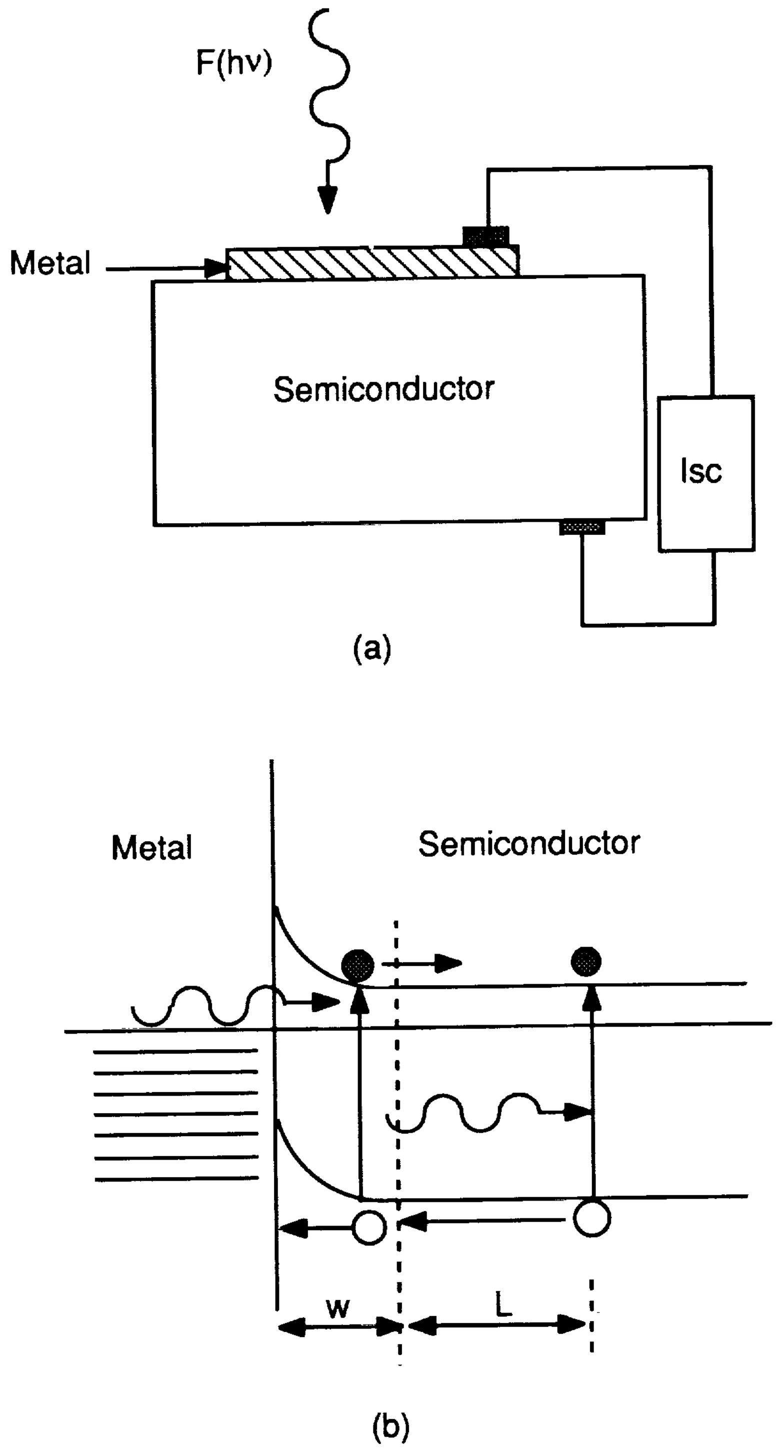


Figure 7. (A) Measurement of Short-Circuit Current for a Schottky Barrier Device; (B) The Associated Band Diagram.

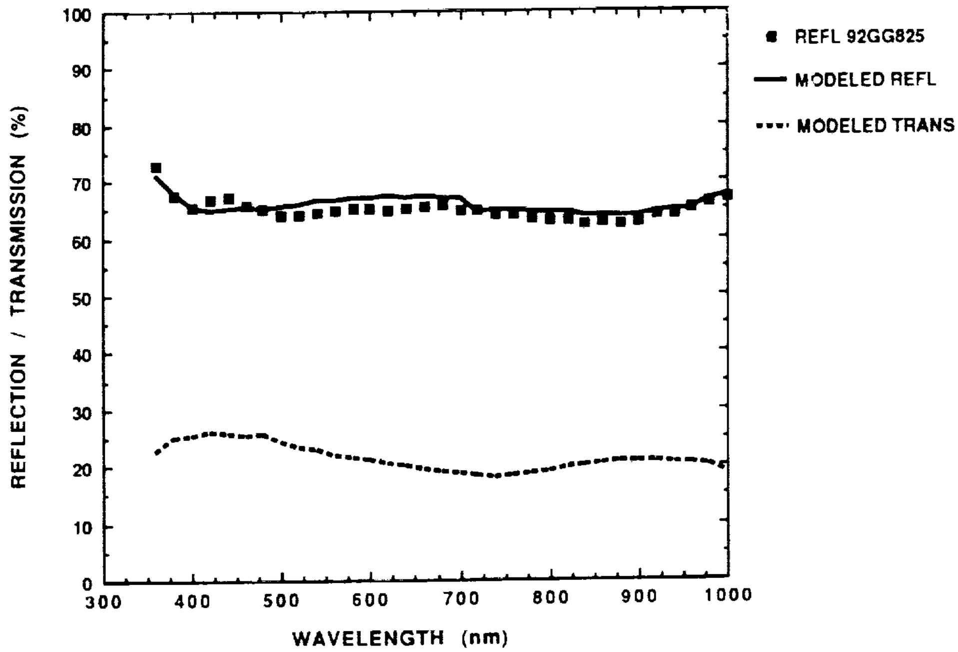


Figure 8. Measured reflection from 90Å Al film on n-GaAs with Modeled reflection and transmission from n and k of Al film deposited on quartz witness.

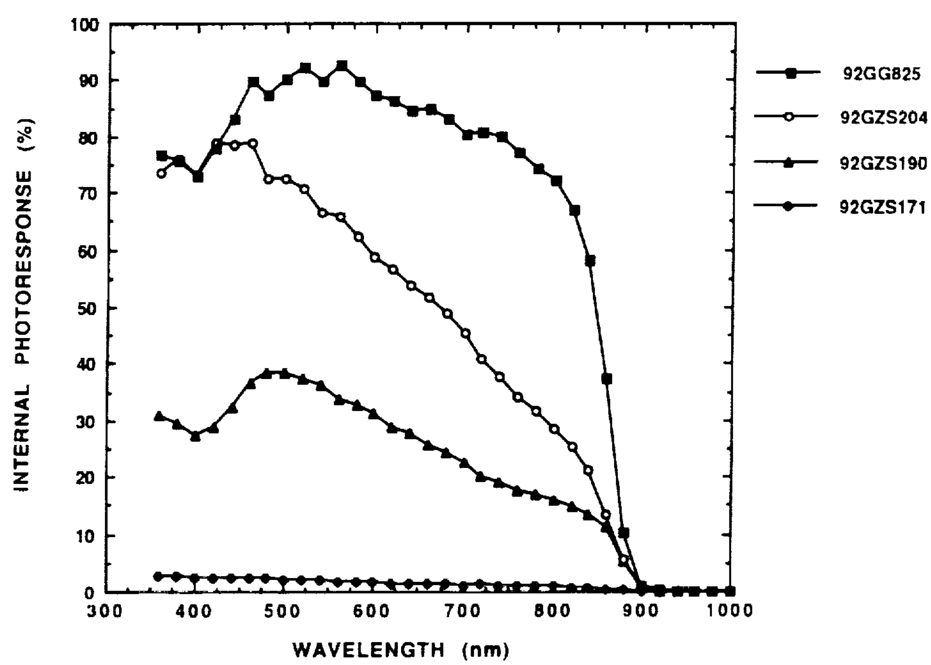


Figure 9. Internal Photoresponse for Al/GaAs Schottky Barriers. The GaAs Films were Grown on ZnSe/Si Substrates.