Phase Equilibrium Modeling for High Temperature Metallization on GaAs Solar Cells*

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Recent trends in performance specifications and functional requirements have brought about the need for high temperature metallization technology to be developed for survivable DOD space systems and to enhance solar cell reliability. The temperature constitution phase diagrams of selected binary and ternary systems have been reviewed to determine the temperature and type of phase transformation present in the alloy systems. Of paramount interest are the liquid-solid and solid-solid transformations. This data is being utilized to aid in the selection of electrical contact materials to gallium arsenide solar cells. Published data on the phase diagrams for binary systems is readily available [refs. 1-5]. However, information for ternary systems is limited. A computer model is being developed which will enable the phase equilibrium predictions for ternary systems where experimental data is lacking.

Introduction

The challenge to obtaining high temperature contacts to solar cells is to control the diffusion properties of the contact metals. Commonly used contact metals such as Ag and Au diffuse considerable distances in GaAs and if allowed to reach the junction (≤ 0.5 μm for space cells) considerable performance degradation will result. Diffusion barriers developed by Varian [ref. 6] and Spire Corporation [ref. 7] have demonstrated stability up to 500°C and 550°C, respectively for 5 minutes. At higher temperatures, dissociation of GaAs occurs and puddling of liquid Ga becomes the chief failure mechanism. A second problem at high temperatures (> 500°C) is the direct reaction between the GaAs compound and other elements to form ternary or more complex compounds or alloys.

GaAs decomposes into an arsenic vapor phase and an elemental liquid Ga phase which readily reacts with electrical conductor materials such as Au, Ag, Cu, or Al. The GaAs decomposition is resolved by applying an AlGaAs capping layer (see figure 1) to prevent losing arsenic via the vapor phase. The direct metallurgical reaction between GaAs and another element/metal is best addressed by choosing metals which prevent or limit the reaction.

Approach

Our approach for selecting contact materials is to use the equilibrium temperature constitution phase diagrams. These phase diagrams show the metallurgical phases occurring in the alloy system of interest. Of particular interest are those ternaries containing gallium, arsenic, and one of the electrical contact metals. Extensive compilations exist for binary systems [refs 1, 2, and 3] but a limited number of phase diagrams for ternary systems are available [refs. 8 and 9]. Using the data in the binary diagrams to determine the necessary thermodynamic data, we can construct the appropriate ternary phase diagram. Computational methods are being developed and utilized to predict/calculate the ternary boundaries. These calculated ternary phase boundaries are performed using thermodynamic models of the free energy of the ternary phases and where necessary, the calculations supplemented with experimental data. These experimental measurements are utilized in an iterative manner with the computations to improve the reliability of the phase diagrams. The projections of the ternary phase diagrams are compared to known experimental results at selected alloy compositions to verify the projections from the binary diagrams.

Phase Diagram Calculations

A FORTRAN IV code for calculating the equilibrium phase diagrams of binary systems containing intermediate compound phases has been developed. The computations of the phase boundaries for this particular class of phase diagrams requires, as input, the following data:

1. The melting temperatures and heats of fusion of the elements.
2. The composition, melting temperature, and heat of fusion of the compound.
3. The binary quasi-chemical interaction parameter for the liquid and solid phase.

A phase diagram calculated with this model is shown in figure 2. Since the primary purpose of this model is to utilize the phase diagram to determine the liquid-solid transformation temperatures, only those phase boundaries involved in a liquid-solid reaction are calculated. Those boundaries are shown as solid lines in figure 2. The solid-solid transformations are shown as dotted lines. Two eutectic transformations occur in this type of phase diagram and are shown as e1 and e2. The temperatures of these eutectic reactions are the temperatures at which liquid-solid transformations will occur on heating in this type of system. In all instances, these temperatures occur below the melting point of either the compound or the elements.

Before the model for figure 2 could be developed, a code had to be written to calculate the binary eutectic phases. This requires that the code calculates the liquidus, solidus, and solvus phase boundaries as well as the temperature and composition of the eutectic transformation. The binary eutectic is one of the basic building blocks of

our modeling. By combining it with the phase diagram of binary systems with intermediate binary phases, ternary gallium arsenide phase diagrams can be calculated.

Figure 3 is a simple binary eutectic phase diagram. There are three single-phase regions, the liquid phase and two solid phases, which are labeled as the α and β phases. In addition, three two-phase regions exist, the α+liquid region, the β+liquid region, and the $\alpha + \beta$ region. The intersection of the two liquidus boundaries, e1, locates the eutectic temperature and composition. The temperature and type of transformation for a combination of materials can be determined by analyzing the phase diagram.

Preliminary Model Verifications

The results of the calculation for the Ga-Zn binary eutectic system are shown in figure 4. Because of the large difference between the melting points of Ga and Zn, the eutectic point (e1) is displaced toward the lower melting element, Ga. In comparing figures 3 and 4, it is seen that the liquidus 1 and solidus 1 boundaries are almost completely lost and the solidus 2 boundaries differ. The behavior of the solidus boundary is referred to as exhibiting retrograde solubility [ref. 3]. This means that the solubility of gallium in solid zinc increases as the temperature decreases from the melting point of zinc. At a temperature between the melting point and the eutectic temperature, the solubility reaches a maximum value and then decreases as the temperature continues to decrease.

Figure 5 is previously published experimental data for the Ga-Zn binary eutectic. Comparing this diagram to the one generated by our model (figure 4) shows almost identical results and thereby indicating that our model is accurate.

Discussion and Conclusion

Verification of the accuracy of our model for binary systems with intermediate compound phases is necessary before proceeding to the ternary systems. This will be done by comparing diagrams from our model to published experimental data. Results to date indicate that our model should be accurate and will therefore be an invaluable tool in theoretically determining the thermal stability of ternary systems prior to any experimental activity. Presently, an Edisonian approach is the way that high temperature metallization for GaAs solar cells is being developed.

References

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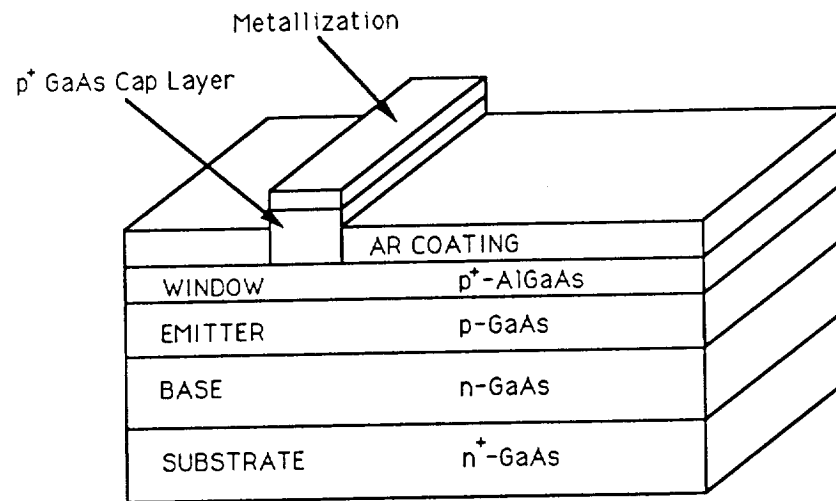
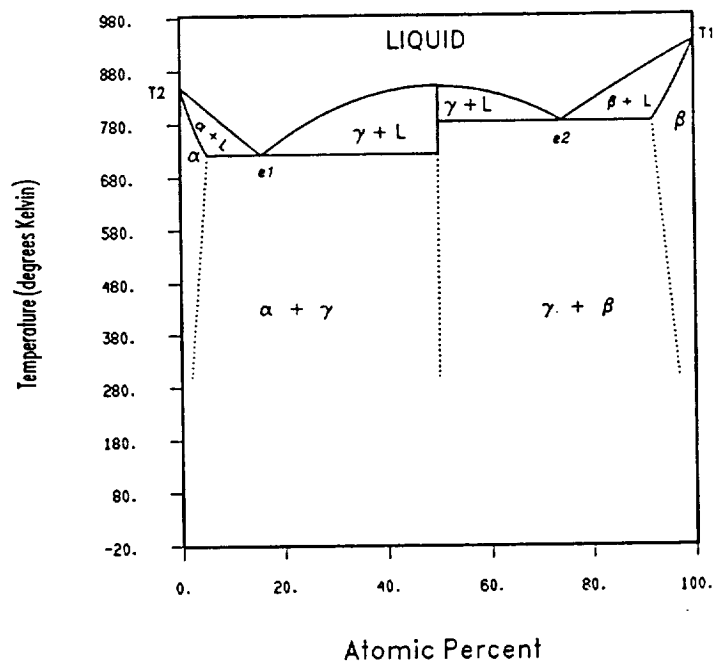Figure 1 - Schematic of a typical GaAs solar cell with grid contact.

Figure 2. - Phase diagram for a binary system containing an intermediate melting compound phase.
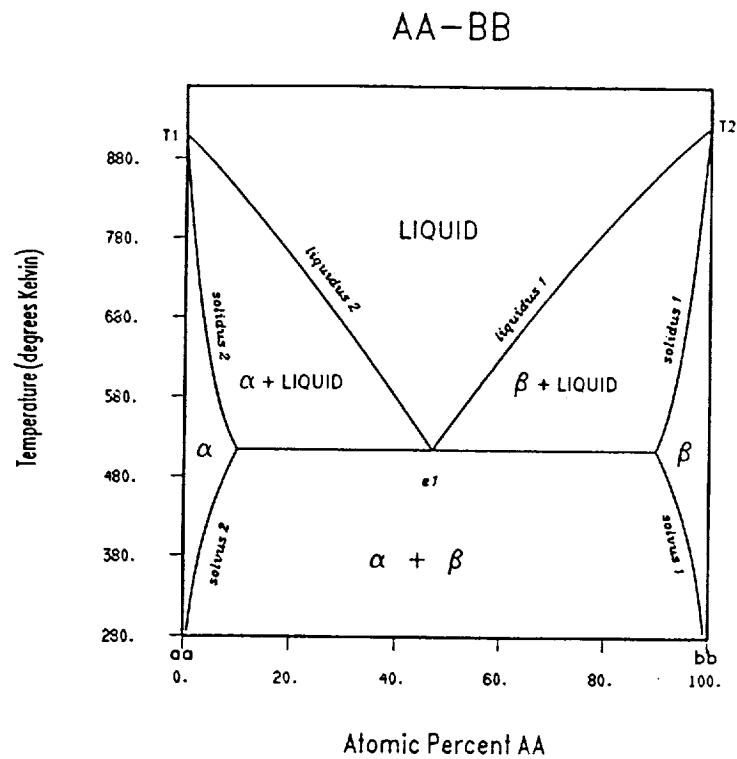
AA—BB

Figure 3. - Binary eutectic phase diagram.
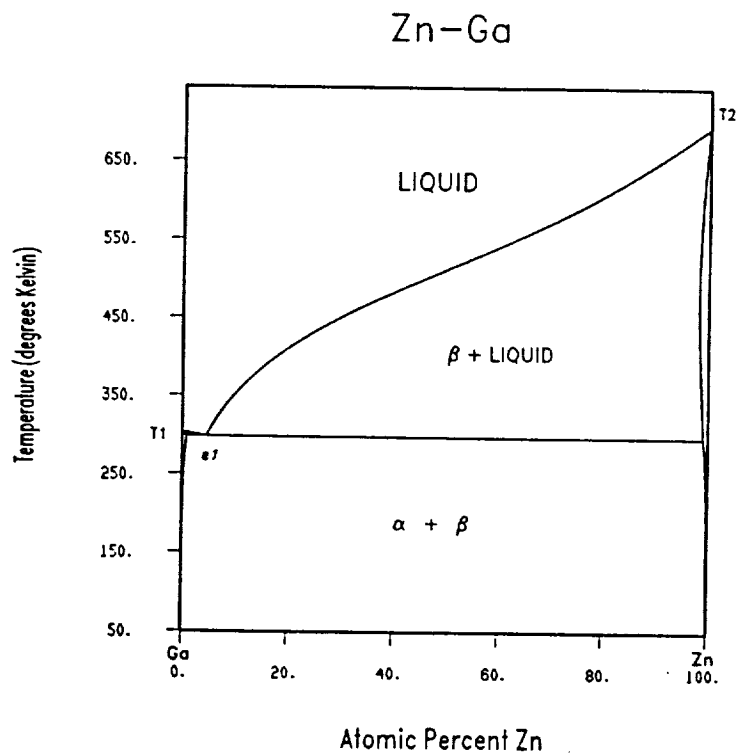
Zn—Ga

Atomic Percent Zn

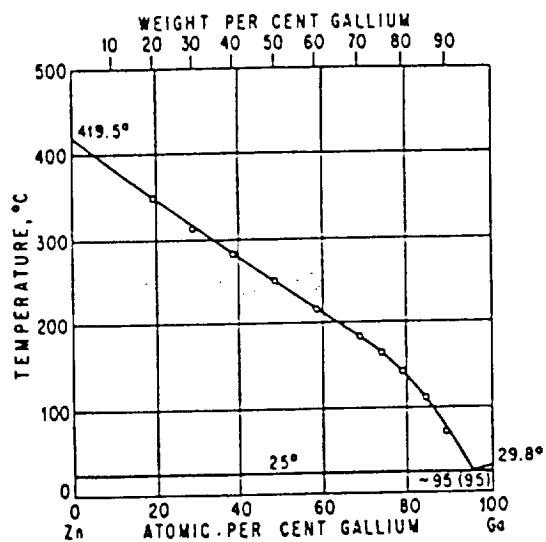Figure 4. - Binary eutectic phase diagram for the gallium-zinc binary system.

Figure 5. - Experimental phase diagram for gallium-zinc (ref. 3).