FIG. 2. Plot of (depletion capacitance)$^{-2}$ vs applied bias voltage for the diode whose photoresponse appears in Fig. 1. The built-in voltage is 1.28 eV for this diode.

photoelectrons from the gold into the GaP. With regard to photoresponse measurements we would like to point out an incorrect statement in Ref. 1 to the effect that the photocurrent in n-type GaP–gold diodes is due to hole rather than electron injection.

Figure 2 shows a plot of the reciprocal square of the depletion capacitance vs bias voltage for the diode whose photoresponse curve is shown in Fig. 1. The intersection of this plot with the voltage axis yields the built-in voltage, in this case about 1.28 eV. Similar plots for the other diodes yielded values between 1.25 and 1.35 eV. If image corrections are neglected, the built-in voltage should be less than the barrier height by an amount ξ_n, where ξ_n is the energy difference between the Fermi level and the bottom of the conduction band. ξ_n has been estimated at 0.03 eV for our GaP samples, and, therefore, within experimental error, the barrier heights determined by the photoresponse and capacitance methods agree closely.

Logan and White report that their depletion capacitance measurements on n-type GaP–gold junctions yield values for the built-in voltage between 1.3 and 1.9 eV. They attribute this phenomena to surface states. It is also possible that this wide variation was due to the presence of thin interfacial contaminating films, particularly in the case of the diodes whose measured built-in voltage was greater than 1.3 eV. Following the analysis of Goodman,[6] we have performed calculations which show that contaminating films with thickness of the order of tens of angstroms are sufficient to cause variations of a volt or more in the barrier height as determined by the depletion-capacitance data. We have measured the depletion capacitance of junctions prepared by vacuum evaporation of gold onto GaP in an oil-diffusion vacuum station. These measurements show exactly the variation in barrier height which one would expect from the presence of a contaminating interfacial film on the basis of Goodman's analysis. Barrier heights in the range of 2.0 to 2.5 eV were measured in these cases, and presumably the contaminating films were due to the small amount of unavoidable oil vapor present in this vacuum system. It is interesting to note that Goodman's analysis predicts a linear relationship between the reciprocal square of depletion capacitance and voltage, even for the cases where an interfacial film is present. Our experiments have borne out this prediction exactly.

The photoresponse of the diodes prepared in the oil-diffusion system was relatively unaffected by the presence of contamination; in general, the fit of the experimental points to a Fowler function for these diodes was not as good as for the diodes prepared in the Varian system, but within experimental error, the measured barrier height remained essentially the same. It is significant to note that diodes prepared in the Varian system using GaP crystals which had been exposed to the atmosphere for an hour or longer behaved the same in every respect as the diodes prepared in the oil-diffusion system, except that values of the built-in voltage determined from the capacitance measurements were generally between 1.5 and 2.0 V. Since Logan and White report that they used diodes prepared from GaP that had been allowed to stand in air for 1 h or so, we suggest that the cause of the observed variation in values of built-in voltage may have been due to the presence of an interfacial film in the junctions.

The current–voltage characteristics of the diodes prepared in the Varian system by the first method were found to obey closely the relation

$$I = I_0 \exp[qV/nkT],$$

where n was typically in the range 1.15–1.25. The built-in voltage determined from the current–voltage characteristics was between 1.1 and 1.3 eV for all the diodes, and in every case was less than the corresponding value determined from the capacitance data.

From the photoresponse and capacitance measurements described in the preceding paragraphs, we have inferred a value of 1.30 eV for the n-type GaP–Au barrier height. Also, in view of our measurements and calculations for diodes prepared from "contaminated" GaP samples, we are inclined to attribute variations in built-in voltage determined from capacitance data to the presence of interfacial films, rather than to surface states as suggested by Logan and White.

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Adhesion of Vapor-Deposited Aluminum to Lime-Soda Glass

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THE production of an adherent vapor-deposited metal film on a glass substrate has been accomplished with various degrees of success by a wide variety of techniques. The literature on the subject has been extensively surveyed by Holland.[1] Further systematic work has been carried out by Benjamin and Weaver.[2]

The most significant conclusion to date is that the bonding takes place by the formation of a metal-oxide transition layer between the metal and the glass. This conclusion came largely as a result of the observation that those metals that tend to adhere to glass are the metals that oxidize readily in air, and those metals that adhere hardly at all do not oxidize readily in air.

In spite of all of the effort directed towards production of thin films of metal on glass there is yet little understanding of the mechanical properties of the film. The adhesion of the film to glass is frequently measured by the cellophane tape method. If the metal film remains attached to the glass substrate after attempted removal with adhesive cellophane tape, the film is considered to be an adherent film. Another qualitative method, devised by Benjamin and Weaver,[3] tests the strength of the metal film–glass interface in shear; a smooth steel pin is drawn over the metal film and the vertical load on the steel pin is increased until the film separates from the glass.

In the present work, the mechanical strength of vapor-deposited aluminum films and the strength of adhesion of the films to glass was tested by a direct tensile method. Adherent aluminum films about 250 Å thick were vapor-deposited on fresh soda-glass microscope slides (0.75 mm thick). After deposition was completed, a clean gold sphere of 3-mm diameter was pressed against the aluminum at room temperature, then pulled to separate it from the glass. In four consecutive cases the gold–aluminum bond, the

aluminum film, and the aluminum–glass bond were strong enough to pluck nuggets of glass from the microscope slides.

The production of adherent films requires considerable care. An outline of the glass preparation and evaporation conditions is given. Only four runs or cases are here reported but adherent films were produced on many other occasions at will, without measuring film strengths.

If the assumption of a metal oxide or other transition layer is correct, the production of an adherent film begins with the removal of all foreign matter including gases from the surface of the glass. The work of Langmuir, Manley,[4] and others on the adsorption of gases on solid surfaces shows that the strong bonding forces of a substrate do not extend beyond one monolayer of gas upon the surface. Thus the surface must be cleaned before deposition so that at most only a small fraction of a monolayer remains. A high vacuum is sufficient to remove the upper layers of gas and in accord with the several adsorption isotherms of Langmuir, Pashley,[4] and others, heating in a vacuum should partially remove the monolayer.

The surface should remain clean for some time while a proper mixture of metal vapor and oxygen arrive at the glass surface. After several Angstrom units of thickness of metal oxide have formed, the ratio of oxygen to metal vapor should decrease to zero after which pure metal alone condenses.

In this work the glass was first degreased by washing with ordinary handsoap and by rinsing in water and isopropynol. The glass was degassed by heating to between 540° and 650°C (1000° and 1200°F) for four minutes in a vacuum of 10^{-6} Torr. This treatment removed surface gases and probably also reduced the concentration of gases just below the surface of the glass as well.

At the end of the degassing cycle the glass was allowed to cool by radiation. At this point the partial pressure of H_2O and CO_2 is very low because of the "pumping" action of the liquid nitrogen trap. There is very likely a higher proportion of O_2 than in the atmosphere, which is desirable. More oxygen can be admitted and indeed was in the early work. But the result usually was a deposited layer of low density and strength. The weak films failed within the film thickness rather separate from the glass in the tensile test. To obtain a high-density film another procedure was used.

After the glass had cooled only 45 sec from the degassing temperature, a film 200 Å thick was deposited. The glass was immediately reheated to 537°C (1000°F) and held for three minutes. This probably allowed sintering and oxide formation in the metal film. Then the glass was allowed to cool for 30 sec after which a second layer was deposited on the first layer.

Within 30 sec after the second layer of aluminum was deposited on the glass a clean gold sphere was pressed against the metal film with a force of 240 g (8.5 oz), with a minimum of impact. The pressing force was removed and a separating force was applied. In four consecutive cases the test ended with the removal of a nugget of glass from the glass plate.

In two of the cases the separating force was found to approach 280 g (10 oz). In the other two cases the separating force was near 140 g (5 oz).

The stresses resulting from the tensile test cannot be determined with significant accuracy. However certain estimates can be made. The diameters of the cavities from which the glass nuggets were removed were about 5 mm (0.02 in). Thus for the four cases the average tensile stress in the contact area was between 1000 and 2000 psi.

Just as in the case of compressive contact, the stress distribution across the area of contact is not uniform. Johnson finds the maximum stresses in the adhesion case to be tensile and infinite.[5] McFarlane and Tabor in their work on adhesion of metals find the maximum adhesion stress to be at the rim of the contact area and it is considerably higher than the average stress.[6] Whatever the conclusions from theoretical considerations may be, it is logical to assume that the stresses in the contact region are not much greater than the simple tensile strength of the failed member, in this case

the glass. The tensile strength of the type of microscope slides used was found to average about 20 000 psi, as determined by the standard bend test. The adhesion stresses must have been nearly 20 000 psi to initiate failure in the glass.

The tensile test shows that the gold–aluminum adhesion strength, the strength of the vapor deposited layer, and the aluminum–glass adhesion strength in this work exceeded 1000 psi and approached 20 000 psi. This is considerably higher than previously reported.

Other technological conclusions can be drawn.

a. Good adhesion can be accomplished between a vapor deposited metal film and a clean metal. No heating or rubbing is required, contact is the only requirement.

b. Dense and strong vapor deposited layers of aluminum can be obtained by sintering and oxide formation.

c. The production of adherent vapor deposited films of aluminum is critically dependent on the removal of adsorbed gases from the glass.

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CsCl-Type Compounds in Binary Alloys of Rare-Earth Metals with Zinc and Copper*

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THE CsCl-type structure has been previously reported in alloys of copper with yttrium, gadolinium, and erbium,[1] and of zinc with lanthanum, cerium, and praesodymium.[2] The present investigation has uncovered five additional phases in copper–rare-earth alloys and nine in zinc–rare-earth alloys.

TABLE I. Lattice parameter of compounds of B2-type structure of rare-earth elements with copper and zinc.

Compound	Lattice-parameter (Å)	
	Present work	Previous work
YCu		3.476 ± 2 [a]
SmCu	3.528 ± 2	
GdCu		3.505 [a]
TbCu	3.480 ± 4	
DyCu	3.460 ± 3	
HoCu	3.445 ± 2	
ErCu		3.432 [a]
TmCu	3.414 ± 1	
YZn	3.577 ± 3	
LaZn		3.759 [b]
CeZn		3.704 [b]
PrZn		3.678 [b]
NdZn	3.667 ± 2	
SmZn	3.627 ± 1	
GdZn	3.602 ± 4	
TbZn	3.576 ± 4	
DyZn	3.563 ± 3	
HoZn	3.547 ± 3	
ErZn	3.532 ± 3	
TmZn	3.516 ± 3	

[a] See Ref. 1.
[b] See Ref. 2.