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The influence of substrate characteristics on the contact angles between liquid gallium and gallium arsenide crystals

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Parameters influencing the interfacial interaction between liquid gallium and single crystalline gallium arsenide were investigated under vacuum by means of the sessile-drop technique over the temperature range ~ 30 to 200° C. In addition to their dependence on the anisotropy of the {111} planes, contact angles in the Ga(l)/GaAs(s) system were found to be sensitive to the degree of misorientation and the direction of tilt of these planes. Furthermore, contact angles were found to be dependent on the size of the liquid drop and on the surface roughness of the substrate. In agreement with theoretical expectations the measured angles increased with increasing roughness of the GaAs surfaces. However, these angles were found to be unaffected by the presence of N_2, Ar, and He atmospheres, and by the nature and concentration of charge carriers in the substrate.

1. Introduction

The characteristics of solid-liquid interfaces have been the object of considerable attention over the past few decades. Among the numerous types of investigations, those utilizing the sessile-drop technique have been largely instrumental in providing a better understanding of the parameters influencing such considerations as adhesion [1], ceramic-to-metal bonding [2], and ohmic contact in electronic devices [3]. Of interest in any or all of these considerations are those characteristics of the solid substrate which have a significant influence on the liquid-solid interaction.

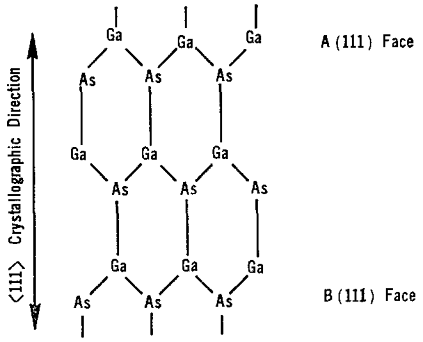

Figure 1 A schematic representation of the {111} planes of GaAs.

In a previous publication [4] we reported the anisotropic nature of the contact angles between liquid gallium and the {111} planes of gallium arsenide. This compound, with its zincblende structure has its {111} planes alternately occupied by Ga and As atoms as shown schematically in Fig. 1. Thus this alternating chemical nature of these parallel planes gives rise to an appreciable difference in the contact angles between liquid gallium and the GaAs crystals. In this paper we report the results of an investigation on the influence of surface roughness and surface misorientation on the measured contact angles.

The question of misorientation becomes rather interesting when one realizes that the *A*(111)

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faces of gallium arsenide had contact angles with liquid gallium which differed by about 30° from those measured on the $B(\bar{1}\bar{1}\bar{1})$ faces. With a difference of this magnitude it would be reasonable to expect significant changes in the contact angle as the crystalline orientation of a (1 1 1) plane, for example, shifts towards the $(\bar{1}\bar{1}\bar{1})$ plane via the (1 1 0) or (1 0 0) intermediate planes.

Wenzel [5, 6] had developed a relationship between the macroscopic roughness of a solid surface and the angle of contact (and thus the degree of wetting) between a liquid and the solid surface. Of the several consequences of Wenzel's relationship, that concerning the direction of change in the values of the contact angle as influenced by surface roughness is of immediate interest here [7]. For contact angles $\theta < 90°$ the apparent angle, θ', decreases as the surface roughness increases. Conversely, for $\theta > 90°$ the liquid appears to better wet the solid as the latter's roughness decreases. Thus the contact angles between liquid Ga and GaAs are expected to follow the latter behaviour since their values were found to be greater than 90° over the temperature range ~ 30 to 480°C [4].

2. Experimental methods

The apparatus used to measure the contact angles between gallium and GaAs in this work has been adequately described in a previous paper [4]. Minor modifications made it possible to bleed into the system inert and semi-inert gases while maintaining a given ambient pressure. Confidence in the results obtained with this apparatus has been established in accordance with the previously described experiments. Temperatures were measured by chromel/alumel thermocouple which were in physical contact with the substrate.

To avoid significant contributions to the measured angles which can result from the oxidation of the liquid drop, each individual experiment utilized a freshly prepared gallium droplet. The procedure for the preparation of each droplet is made relatively simple by the fact that gallium has an exceptionally low melting point, 29.78°C. A small piece of gallium was initially cut from a 99.9999% pure ingot which was then washed with acetone and placed near the edge of a 7.5 cm diameter watch glass containing a few cm^3 of dilute HCl. A clean heated spatula was used to melt the gallium piece and thus causing the liquid to role down the side of the watch glass into the acid. By this procedure it was possible to obtain nearly perfect spherical droplets which then solidified while settling down in the acid solution. Each droplet was then removed from the acid solution, washed first with distilled water, and then rinsed with acetone before placing it on the prepared substrate. Contact angle measurements usually commenced within a few minutes after the droplet had been prepared.

Single crystals of p- or n-type semiconductor grade GaAs, manufactured by Monsanto Company of St Louis, were oriented by X-ray methods and cut into approximately 2 mm thick wafers along the (1 1 1), (1 0 0) and (1 1 0) planes by means of a high speed diamond saw. For the purpose of studying the influence of crystallographic misorientation on the contact angles, several wafers were cut along planes deviating from (1 1 1) by 5° increments toward either the (1 0 0) or (1 1 0) planes. Laue patterns of these cut wafers showed them to have the desired orientation within approximately ± 1°. Identification of the $A(111)$ and $B(\bar{1}\bar{1}\bar{1})$ faces of GaAs was accomplished by a chemical etch consisting of one part by volume HNO_3, six parts HCl, and ten parts H_2O [8]. All substrates identified in this manner were then polished (to variable finishes for the influence or roughness experiments) and chemically etched to remove the strained surface layer. Polishing of the specimens was accomplished by first using No. 600 paper followed by finer paper and culminating with a series of diamond grit ranging down to $\frac{1}{4}$ μm size. Standard polishing techniques gave mirror-like surfaces which were then washed with soap solution and rinsed with distilled water and acetone. To remove the effects of polishing, in the form of strain in the surface layer of the substrate, each wafer was etched with a hot solution of 1:1 conc H_2SO_4 and 30% H_2O_2.

The surface roughness, defined as the centre-line-average height (CLA), was determined by a Taylor-Hobson Talysurf 4. The surface roughness values reported later are the averages of four measurements made on each side. The length traversed during each measurement was 0.63 cm. These measurements were made randomly over each surface after the completion of the contact angle measurements.

Sessile-drop measurements were normally made under a background pressure of better than 5×10^{-6} Torr and at temperatures ranging from about 30 to 200°C. At any given temperature, contact angles were measured every 5 min to determine any time dependence on these measurements. Time durations of about 15 to 60 min were allowed to ensure the existence of steady state conditions. No visible interactions between the liquid drop and the substrate could be observed over the temperature range covered in this work. However, at temperatures approaching 500°C severe interactions could easily be observed.

3. Results

To establish the influence of the drop size on the measured contact angles, a series of experiments were conducted utilizing drops ranging in size from about 0.5 to 4.0 mm diameter. Fig. 2 depicts the results of these experiments on a (1 1 1) oriented substrate which was polished with 1 μm diamond paste.

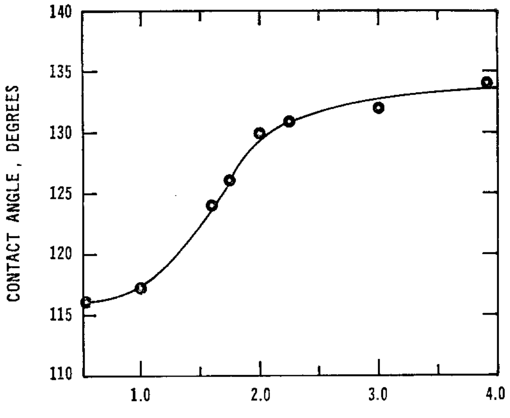

Figure 2 The variation of contact angle with drop size in the system Ga(l)/GaAs(s).

It appears that in this system (Ga/GaAs) the size of the droplet has s significant influence on the measured angle, especially in the region between about 1.0 and 2.0 mm diameter. Thus in all subsequent experiments the droplets were prepared with uniform diameters of ~ 1.0 mm.

Fig. 3 shows the variation of the contact angle, θ, with the degree of roughness of the substrate. The angles measured, using droplets of the same size, varied between about 118° to about 131° depending on the roughness of the substrate. Having thus established the variation of the contact angle with the size of the droplet and the roughness of the substrate, all subsequent experiments were carried out with a 1 mm diameter droplet and surfaces polished to give the lowest values of θ, i.e. with a 1 or $\frac{1}{4}$ μm diamond paste as a final polish (see Fig. 3).

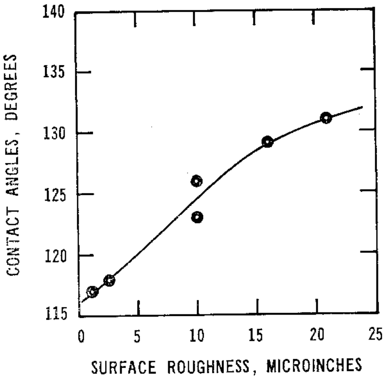

Figure 3 The influence of surface roughness on the wettability of gallium on gallium arsenide.

The results of the polarity dependence of θ on the nature of the {1 1 1} plane are presented in Table I, from which it can be seen that, as published previously [4], a difference of about 30° exist between the $A(111)$ and $B(\bar{1}\bar{1}\bar{1})$ faces of GaAs over a temperature range extending to over 200°C. Fig. 4 gives the results of measurements of θ on planes which were cut from a (1 1 1) plane with 5° increments towards the (1 1 0) and (1 0 0) planes. The terminal values on each curve is based on the results of the previously mentioned study.

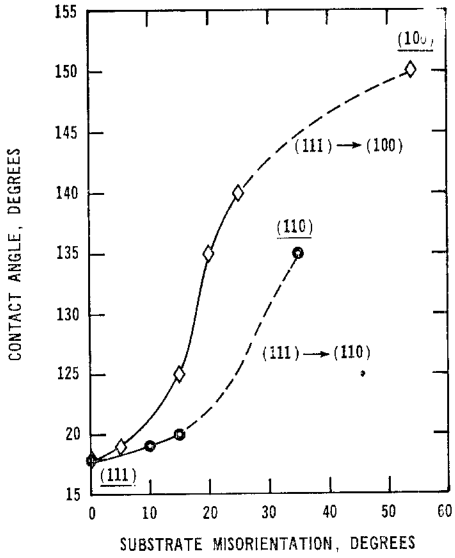

Figure 4 The influence of crystallographic misorientation of (1 1 1) oriented GaAs substrates on the contact angle with Ga(l).

TABLE I Contact angles between liquid gallium and $\{111\}$-oriented GaAs crystals

T (°C)	θ (degrees)
(1 1 1) face	
22*	114
80	114
108	116
211	114
$(\bar{1}\bar{1}\bar{1})$ face	
25*	142
26*	140
100	142
204	141

*Values measured after cooling to ambient temperatures.

Several attempts were also made to determine the possible influence of additional parameters which may be anticipated to have an influence on the experimentally determined contact angles. Of these the influence of the ambient gas was investigated. Contact angles were measured on the A(1 1 1) faces under a 10^{-4} Torr atmosphere of N_2, Ar, and He gases. The average values of the results of these experiments (118, 118, and 116, respectively) did not differ significantly from those obtained under vacuum at 200° C. Furthermore, another series of experiments demonstrated that essentially identical results are obtained with n- or p-type specimens of GaAs. P-type specimens with a carrier concentration of 2.3×10^{15} cm^{-3} gave (within $\pm 2°$) identical results to those obtained with n-type GaAs having a carrier concentration of 1.1×10^{16} cm^{-3}.

4. Discussion

Based on a consideration of the proposed model of Gatos and Lavine [9, 10], it would be anticipated that the As-face $(\bar{1}\bar{1}\bar{1})$ would give a stronger interaction with the gallium and, hence, a smaller θ. The present results are contrary to this anticipation, and may very well be influenced by an unavoidable degree of adsorption of the ambient gases on the liquid phase. The insensitivity of the contact angle to the nature of the ambient gases nitrogen, argon and helium, and the close agreement between these angles with those obtained under vacuum may be taken as a possible indication of the role of adsorption. What is significant, however, is that such possible surface changes did not mask the influence of either the polarity of the $\{111\}$ planes or the degree of misorientation of these planes on the contact angles. This latter observation may still be in agreement with the Gatos and Lavine model if one assumes that adsorption of the ambient gases occurred nearly exclusively on certain crystalline faces, e.g. the $(\bar{1}\bar{1}\bar{1})$ planes.

A mathematical treatment of the contact angles on an idealized rough surface has been developed by Dettre and Johnson [11, 12]. In accordance with such an approach, the Wenzel roughness factor, r, defined by

$$r = \frac{\cos \theta'}{\cos \theta} \tag{1}$$

in which θ' and θ are the apparent and real contact angles, respectively, is expected to be an increasing function of θ' for $\theta' > 90°$ [5]. In Fig. 5, this relationship is depicted on the basis of a real value, θ, obtained from extrapolating the curve of Fig. 3 to "zero roughness". Recognizing that the value of θ obtained in this fashion is not exact, the curve of Fig. 4, therefore, represents a trend which is consistent with the expectation cited above.

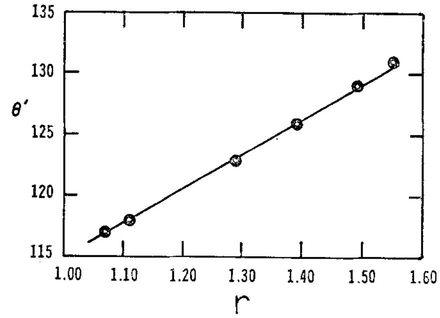

Figure 5 The apparent contact angle versus Wenzel's roughness ratio.

As depicted in Fig. 4, the influence of misorientation of the (1 1 1) plane on the contact angle with gallium is highly dependent on the direction of the tilt at relatively large misorientations. At misorientations of up to about 10°, however, the results appear to be essentially identical for surfaces tilted towards the (1 0 0) or the (1 1 0) planes. The change in contact angles of misoriented (1 1 1) planes is, of course, a result of the change in the atomic composition of the tilted surfaces and the degree to which these newly formed surfaces had been influenced by the ambient gases during their preparation.

5. Conclusions

The contact angles between gallium arsenide substrates (prepared under ambient conditions) and liquid gallium were found to be highly sensitive to certain interface conditions and essentially independent of others:

1. The contact angle for the Ga/GaAs system was found to be strongly dependent on the drop size of the gallium. Over the range of drop sizes investigated, the cosine of the angle increased by a factor of about 1.6.
2. In accordance with theoretical expectations for obtuse contact angles, increasing surface roughness caused a decrease in the wettability of the gallium arsenide.
3. At relatively low crystallographic misorientation of the (1 1 1) planes ($\sim 10°$), the contact angles are essentially unchanged. However, at larger tilt angles the contact angles increase significantly with a strong dependency on the direction of the tilt.
4. Apparently the contact angles are not dependent on the nature or the concentration of the charge carriers in the gallium arsenide substrates. Contact angles on p- and n-type GaAs were identical.
5. Contact angles measured under vacuum (10^{-6} Torr) were essentially the same as those observed under 10^{-4} Torr of nitrogen, argon and helium atmospheres.

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