

# Interaction of liquid and solid gallium with thin silver films: Synchronized spreading and penetration

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## Abstract

The synchronized lateral spreading and through-penetration of liquid and solid gallium (Ga) in supported thin polycrystalline films of silver (Ag) were studied. The spreading and penetration kinetics were presumably controlled by a common mechanism. The spreading rate in the 0.5  $\mu\text{m}$  thick film was found to be constant with time. The activation energies of the process responsible for spreading/penetration of liquid and solid Ga were  $E_L \approx 28.9 \pm 4.8 \text{ kJ mol}^{-1}$  and  $E_S \approx 48.2 \pm 9.6 \text{ kJ mol}^{-1}$ , respectively. Grain boundary grooving, with Ag diffusion out of the groove either through liquid Ga or through solid Ga, was suggested as a possible mechanism of the spreading and penetration. The model proposed reproduced the observed spreading/penetration rates and gave reasonable estimates of the energies  $E_S$  and  $E_L$ .

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## 1. Introduction

The terms grain boundary wetting (GBW) and grain boundary penetration (GBP) refer to the formation and extension of capillary liquid–metal films, grooves or channels along grain boundaries (GBs) in solid metals [1–4]. In contrast to liquid–metal (LM) embrittlement, GBW was observed in many metals in the absence of applied stress [1–6]. GBW represents a kind of intergranular corrosion in liquid metals and may be attributed to dissolution and fast out-of-tip diffusion of solid metal atoms through the LM channels. It is well known that the diffusion coefficient in liquid metals,  $D_L$ , is faster by at least three orders of magnitude than in solid metals ( $D_L \approx 10^{-9} \text{ m}^2 \text{ s}^{-1}$  vs.  $D_S \approx 10^{-12} \text{ m}^2 \text{ s}^{-1}$ ), even around the melting point  $T_m$ , while for  $T < T_m$  the difference can reach many orders of magnitude, the more so the lower the temperature is. Hence, GBW can be fast and can thus

lead to fast degradation of mechanical properties, thermal conductivity and electrical conductivity of the solid metal.

The kinetic mechanism of GBP/GBW is not yet clear. It has been proposed to relate either to fast diffusion-assisted mass transport in liquid stimulated by capillary stresses [5,7], coherent [8] or residual [9] internal stresses, to solid-state self-diffusion [1] or hetero-diffusion [10] into GBs. The rate of GBW/GBP is typically of the order of 1–10  $\mu\text{m s}^{-1}$  [1], which suggests that GBP might cause a grave reliability problem for microelectronic thin films, e.g. contact pads, multilayer under-ball metallurgies and solder barrier layers, which have typically sub-micrometer thickness and experience intimate contact with LMs in the process of soldering. This problem can well be of paramount importance with the transition to lead-free solder alloys, which interaction with GB in thin-film metals occurs at higher reflow temperature of  $\sim 240 \text{ }^\circ\text{C}$  for about 10 s [11].

In general, very little has been published so far in the area of GBW in thin metal films. Furthermore, even for bulk metals, most GBW studies have been performed on simple eutectic systems, while all real solder alloys form

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intermetallic compounds (IMCs) with thin film microelectronic metals. The competition between IMC formation and dissolution rates in this case becomes the critical issue [11,12].

The objective of this work was to study the kinetics and mechanism of surface spreading and through-penetration of liquid and solid Ga in supported thin films of polycrystalline silver. The Ag–Ga phase diagram is presented in Fig. 1 [13,14]. The diagram shows Ga–Ag eutectic ( $L \leftrightarrow \text{Ag}_3\text{Ga}_2 + \text{Ga}$ ) at 99.98 at.% Ga and  $T = 29^\circ\text{C}$ , very close to the melting point of Ga ( $T_m(\text{Ga}) \approx 29.8^\circ\text{C}$ ), and IMCs ( $\zeta$ ,  $\zeta'$  and  $\text{Ag}_3\text{Ga}_2$ ) in ranging from 22.1 to 40 at.% Ga. The solubility limit of Ga in solid Ag at room temperature (RT) is  $C_{\infty\text{S}} = 11$  at.% [14], whereas the solubility  $C_{\infty\text{L}}$  of Ag in liquid Ga is lower than 1 at.% between 30 and  $60^\circ\text{C}$ , the latter being the maximal temperature used in our spreading experiments. The equilibrium solubility  $C_{\infty,\text{Ag}/\text{Ga}}$  of Ag in solid Ga is not known; extrapolation of the liquidus line shown in Ref. [15] yields a rough upper estimate of  $C_{\infty,\text{Ag}/\text{Ga}} \approx 1$  at.%.

Along with the presence of IMCs formed by Ga with Ag, the important reason for selection of Ag–Ga system for investigation of GB penetration and spreading is that Ga is remarkably prone to undercooling and can remain liquid for quite a long time even at a temperature of about  $-10^\circ\text{C}$ , which is  $40^\circ\text{C}$  below its melting point. This specific property of liquid Ga was confirmed recently by Koizumi et al. [16–18] by use of ultrasonic attenuation measurements in an “Al thin film–Ga” system [16]. The wide temperature range of existence of the liquid phase enabled measurements of the GBP rate of Ga across a wide temperature range, thus allowing reliable data on the activation energy of the process to be acquired. Furthermore, the tendency for large Ga undercooling provided an interesting opportunity for comparison between the

GBP/spreading kinetics of heavily supercooled, but still liquid, Ga with the kinetics observed for solid Ga at the same temperature,  $T < T_m(\text{Ga})$ . This opportunity could help clarify the underlying mechanism of GBP. Additional advantages of the selected system Ag–Ga are: (i) low resistivity Ag is a promising thin-film interconnect material for microelectronics; (ii) Ag is a noble metal, thus there is no need for protective atmosphere to prevent its oxidation during the experiments at around RT; and (iii) Ga has a low vapor saturation pressure and thus does not contaminate the equipment.

## 2. Experimental

A 5 N (99.999%) Ag target was used for vacuum ion-sputtering deposition of Ag films on 1 mm thick transparent Corning glass substrates. The films had a thickness  $h = 0.47 \mu\text{m}$ , making them non-transparent to visible light. The grain size  $d \approx 0.1\text{--}0.2 \mu\text{m}$  of the polycrystalline film was measured by atomic force microscopy (AFM). Prior to exposure to Ga, the surface of the Ag film was rinsed with distilled water, acetone and isopropanol, and subsequently dried with pure Ar gas. The Ga was melted by hot air, and small drops of it, with varying initial sizes, were carefully placed on the Ag film.

In order to avoid massive dissolution of the Ag film in Ga, we used drops of liquid Ga that were presaturated, prior to the wetting experiments, with Ag – up to the solubility limit  $C_{\infty,\text{Ga}/\text{Ag}}$  of  $\sim 3$  at.% Ag and even contained some excessive Ag in precipitates. This was done by heating a small volume of Ga together with small chips of Ag (total  $\sim 20$  at.% Ga) for 3–4 h at  $200^\circ\text{C}$ . The presence of Ag-rich precipitates in liquid Ga formed a large Ag reservoir, which guaranteed that the liquid was saturated with Ag, even at the highest temperature of  $60^\circ\text{C}$  used in our experiments.

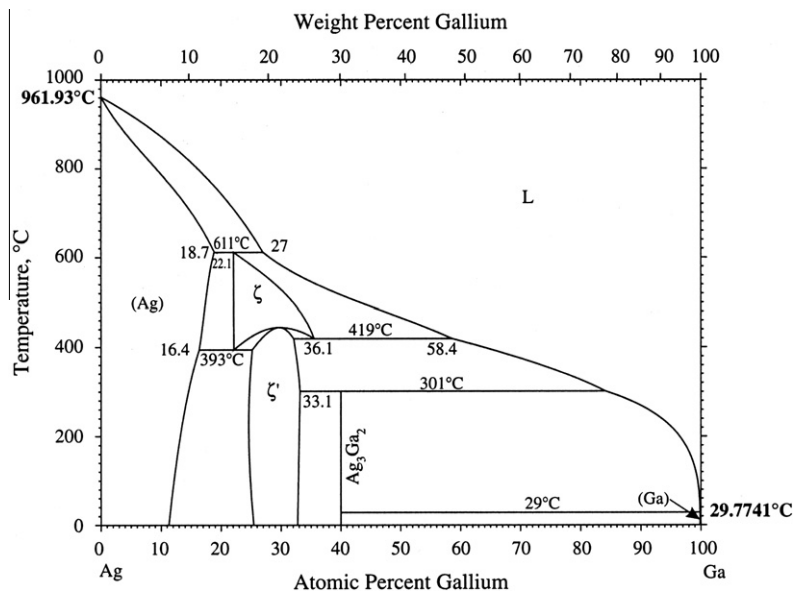


Fig. 1. The silver–gallium binary phase diagram [13,14].

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