

# Electrodeposited Gallium Alloy Thin Films Synthesized by Solid State Reactions for CIGS Solar Cell

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The solid-state reactions of electroplated gallium thin films with copper, gold and molybdenum were investigated using XRD, SIMS, TEM/EDS and linear strip voltammetry. Due to the low melting temperature of gallium metal, the activation energy for gallium diffusion is lower than the other metals used. Hence Ga diffuses faster and reacts to form alloy phases with the other metals investigated. In a thin film stack of Ga with another metals (Me), (Me = Cu, Au and Mo), equilibrium compounds are formed, which compounds form depends on the relative composition and diffusion time. If there is excess Ga, or excess Me, it can further react with the metastable compounds to form an equilibrium compound. In addition, TaN was found to act as an effective barrier layer to gallium diffusion.

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Gallium is an element from the group IIIA. It has been used in the semiconductor and the electronics industries due to its unique exploitable physical properties e.g. electrical and thermal properties.<sup>1–3</sup> There are many applications of gallium in optoelectronics (LED's), telecommunications, aerospace and many other technology products. There has also been a high demand for gallium as a thermal interface material. It is used as highly thermally conducting contact layer between silicon chips and metallic cooling plates.<sup>4–6</sup> Gallium forms compounds in various combinations with aluminum, indium, phosphorus, arsenic, and antimony, (e.g., gallium arsenide and indium gallium arsenide phosphide) with valuable semiconductor and optoelectronic properties.<sup>7,8</sup> Some of these compounds form the basis for electronic devices, for example as light-emitting diodes and semiconductor lasers.

It has recently been reported that gallium plays an important role in achieving high efficiency solar cells if it is incorporated in CuInSe<sub>2</sub> as a partial replacement of indium to form CuInGaSe<sub>2</sub> (CIGS).<sup>9-1</sup> CIGS based solar cells have been considered one of the most promising thin film solar cell technologies. The absorber layer band gap increases from 1.02 eV for CuInSe<sub>2</sub> to 1.1-1.2 eV by a partial substitution of In with Ga, leading to substantial increase in efficiency.9 However, gallium has a low melting point of 29.78°C and thus readily diffuses to form an alloy with other metals e.g. Cu, In, Au, Sn, Zn etc. already at room temperature.<sup>15–19</sup> In photovoltaic applications, e.g. in CIGS fabrication, Ga can be incorporated in the film using both vaccum (PVD)9-11 and electrochemical methods.20-23 Gallium is generally considered a difficult metal to electrodeposit without excessive hydrogen generation at the cathode. The electrode potential required for gallium electrodeposition overlaps with the hydrogen evolution overpotential. As a result the hydrogen evolution causes low plating efficiency and porosity in the film. Surface roughness and microdefects in the film can also become very high due to the hydrogen evolution.

The efficiency of CIGS solar cell, in addition to the other factors, is also dependent on the solid state reaction and stability of Ga in the CIGS layer.<sup>24</sup> In this study, we have investigated electroplated Ga thin films and the alloying of gallium with other elements at room temperature during self-annealing. Stable compounds of gallium form with copper and gold.

## Experimental

A conventional three electrode configuration with a platinum mesh counter electrode and a HglHg<sub>2</sub>Cl<sub>2</sub> (SCE) reference electrode, to which all potentials are referenced, was used. Different substrates (working electrodes) were used in a rotating disk electrode (RDE) system (Pine Research Instrumentation, USA). In all the electroplating and voltammetry experiments, the working electrode was rotated at 540 rpm. The working electrodes consist of (i) a 6 mm diameter gold disk electrode (Pine Research Instrumentation, USA), (ii) PVD copper and (iii) gold seed layers on a glass/Mo and Si(100)/TaN respectively. Except for the standard gold disk electrode, all other substrates were electrically connected through a contact on to the front surface using spring loaded pins.

The electrolyte for gallium plating consisted of 0.25 mol dm<sup>-3</sup> Ga<sup>3+</sup> and 0.5 M sodium citrate of pH  $\geq$  10. The pH was adjusted using a NaOH solution. Deionized water ( $\geq$ 18 MΩ-cm) was used for all solution preparation and rinsing. For both cyclic and linear sweep voltammetry, the potential of the working electrode was controlled using a CHI 660D potentiostate (CH Instruments, Austin, TX, USA). Gallium thin films were electroplated galvanostatically using an AU-TOLAB Galvanostat/Potentiostat with 10 mAcm<sup>-2</sup> current density at room temperature which varied between 19–23°C. These electroplated films were self-annealed at room temperature for a different length of time and then characterized using linear sweep voltammetry (LSV), XRD and microscopy. For the electrochemical identification of the Ga-Me intermetallics LSV was carried out over a potential range of +2V to -2V (SCE) at 0.05Vs<sup>-1</sup> in 0.5M NaOH at different intervals.

The morphology and microstructure of the deposited film were characterized using a Zeiss Leo Scanning Electron Microscope (SEM). A Philips X-ray powder diffractometer (XRD) with a Cu x-ray source ( $K_{\alpha} = 1.54$  Å) was used for phase identification of the Ga-alloy with Cu, Au and Mo. X-ray fluorescence (XRF) was used for thickness measurement of the film. A standard sample for XRF was made and the composition was measured by RBS. A FEI SB 200 Focus Ion Beam (FIB) station was used to prepare samples for cross-sectional SEM and TEM. A JEOL 3000F Transmission Electron Microscope (TEM) equipped with an Energy Dispersive X-ray Spectrometry (EDS) was used for microstructure and chemical composition analysis of the deposit.

Fig. 1 shows a typical cyclic volammogram for the electrodeposition of gallium on gold in 0.25 mol dm<sup>-3</sup> Ga<sup>3+</sup> and 0.5 mol dm<sup>-3</sup>

**Results and Discussion** 

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**Figure 1.** Cyclic voltmmogram of a polished gold substrate in a Ga bath consisting of 0.25 mol dm<sup>-3</sup> Ga<sup>3+</sup> and 0.5 mol dm<sup>-3</sup> sodium citrate with pH  $\geq 10$  at a scan rate 0.05 Vs<sup>-1</sup> from +0.5 V to -2.0 V (SCE). The scaled up I-V in the inset clearly show the onset of cathodic reduction at -0.8 V vs. SCE.

sodium citrate at pH = 13. The potential was scanned from 0.5V to -2.0 V (SCE) at 0.05 Vs<sup>-1</sup>. As the potential is scanned in the negative direction a cathodic current corresponding to the electrodeposition of gallium was observed at -0.8V (SCE). Initially the current is controlled by reaction kinetics but as the potential is increased further a local maximum in current (~11 mA cm<sup>-2</sup>) is reached at a -1.6 V. This is due to mass transport control, i.e. diffusion of the Ga-ions to the electrode surface becomes rate limiting. As the scan continues to a potential more negative than -1.65 V, the magnitude of the current decreases. This is due to the depletion of the Ga-ions in the region adjacent to the electrode. The current eventually reaches a plateau at 10.5 mA cm<sup>-2</sup> when the thickness of the depletion layer (i.e. the region adjacent to the electrode which is depleted of Ga ions) becomes approximately constant. As the potential is made more negative, an increase in current is again observed due to the hydrogen gas evolution  $2H + + 2e^- \rightarrow H_2.$ 

The potential scan is reversed at -2.0V. At -1.5 V the rest potential is reached and no further electrodeposition of gallium occurs. As the potential is scanned to values more positive than the rest potential, the current becomes anodic and the gallium begins to be oxidized according to the reaction  $Ga \rightarrow Ga^{3+} + 3e^{-}$ . The current increases to a peak value and eventually decreases because of depletion of the gallium on the gold surface.

To study the solid state reaction of Ga with copper and gold, a 100-150 nm Ga film were galvanostatically deposited. The substrate was silicon with Mo/TaN/Ta/Cu and TaN/Au deposited by physical vapor deposition. The Ga-deposition was carried out using a bath containing  $0.25\,M\,Ga^{3+}$  and  $0.5\,M$  sodium citrate with  $pH \geq 10$  using  $10\,mAcm^{-}$ current density. Fig. 2a and 2b shows the topography and cross-section images of a typical ~130 nm Gallium on Si/Mo/TaN/Ta/Cu substrate respectively. The surface topography of electroplated gallium on copper shows particle type features (Fig. 2a). The dimensions of these features are in the range of 50-200 nm which is further magnified and shown in the inset of Fig. 2a. These particle type features on the surface indeed caused the film to be rougher which can be seen in the cross-section micrograph (Fig 2b). The surface undulation and these particles, marked by an arrow, can also be seen in the cross-section (Fig. 2b). Fig. 2c shows an x-ray fluorescent profile (energy, eV vs. count) of the sample where 8.04 and 9.26 eV corresponds to Cu-Ka and Ga-Ka respectively. These films were aged at room temperature for different lengths of time and then characterized by XRD and LSV. The XRD data was then correlated with the characteristics anodic peaks obtained by LSV. The LSV was used as an electrochemical spectroscopy method for detecting gallium alloy phases.

A thin film, especially an electroplated film, has large number of defects, e.g. dislocations, vacancies and grain boundaries. These defects can act as a rapid diffusion path. Inter-diffusion at the interface of the two films is possible even at low temperatures due to the presence of these defects. The formation of compounds is presumably the result of both rapid diffusion and lattice diffusion. It has been shown that the inter-diffusion coefficient is highest for the lowest melting



**Figure 2.** (a) Topdown SEM micrographs of ~130 nm gallium thin films electroplated on Si/Mo/TaN/Ta/Cu substrate from 0.25 mol dm<sup>-3</sup> Ga<sup>3+</sup> and 0.5 mol dm<sup>-3</sup> sodim citrate with pH  $\geq$  10 using 10 mAcm<sup>-2</sup> current density at room temperature. Higher magnification image is shown in the inset. (b) Cross-sectional SEM of the film. (c) A typical XRF profile of the film.

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Figure 3. A typical XRD spectrum of Si/Mo/Ta//Ta/Cu substrate. Figures 3b–3d show XRD spectra of ~130 nm gallium films stored at room temperature for  $6.84 \times 10^4$  s,  $4.34 \times 10^5$  s and  $2.59 \times 10^6$  s respectively.



Figure 4. X-ray diffraction spectra of (a) Si/Mo/Ta//Ta//Cu substrate and (b)  $\sim$ 150 nm electroplated gallium on that substrate obtained after 3-hours at 23–25°C.



**Figure 5.** X-ray diffraction spectra of (a) Si/TaN/100 nm gold substrate, (b) and (c)  $\sim$ 150 nm electroplated gallium on this substrate after aging at room temperature between 23–25°C for 1200 s and 7200 s respectively.

metal. This is in agreement with the finding<sup>25</sup> that suggests that the activation energy of self-diffusion of metals is proportional to their melting point ( $T_m$ ): Q = 34  $T_m$ . According to this relationship, the self diffusion at room temperature requires lower activation energy than for the higher melting point metals.

Figure 3a shows a typical XRD spectrum of Si/Mo/TaN/Ta/Cu substrate. Figures 3b-3d shows XRD spectra of ~130 nm gallium films stored at room temperature for  $6.84 \times 10^4$  s,  $4.34 \times 10^5$  s and  $2.59 \times 10^6$  s respectively. During this period the films were held and stored at room temperature (18-20°C). The XRD data (Fig. 3) show that with aging, the intensity of the Cu-Ga alloys phases, e.g. CuGa (101) and CuGa (102) at 20 equals to 35.23 and 44.67 degrees, respectively, increases. However the intensity of the pure copper phases, e.g. Cu (111), Cu (200) and the gallium intermetallics of CuGa<sub>2</sub> (102) at 20 equals to 43.47, 50.67 [JCPDS#03-1018], and 46.55 degrees, [JCPDS # 65-1636] respectively, decreases or disappears (Fig. 3c). This decrease in the intensity of the Cu and Cu<sub>2</sub>Ga phases indicates that the inter-diffusion is still in progress and with further aging time, the remaining copper will react with the remaining CuGa2 and will transform to CuGa intermetallic. Indeed, the XRD spectrum obtained after  $2.59 \times 10^6$  s only shows the intensity for the CuGa phase and there is no intensity for Cu and CuGa2. However, the XRD after after  $5.18 \times 10^6$  s shows no difference compared with the XRD after  $2.59 \times 10^6$  s.

As the gallium is a low melting point metal (29.7°C), a few degrees variation in room temperature plays a key role in its alloying with copper. The gallium films stored at room temperature  $23-25^{\circ}$ C ( $\sim$ 5°C higher than before) show accelerated diffusion and alloy formation with copper in contrast with the film stored at room temperature of 18–20°C. Fig. 4 shows x-ray diffraction spectra of  $\sim$ 130 nm electroplated gallium on Si/Mo/TaN/Ta/Cu substrate obtained after  $1.08 \times 10^4$  s aged at 23–25°C. Due to the aging of the gallium film at  $\sim$ 5°C higher than before, the intensity of CuGa phases appeared higher than the CuGa<sub>2</sub> phases (Fig. 4) at the end of  $1.08 \times 10^4$  s. Whereas the sample aged



**Figure 6.** I-V curves obtained by LSV over a potential ranging from -2V to +2V (SCE) at  $0.05Vs^{-1}$  in 0.5M NaOH. (a) shows I-V curves obtained by LSV of Si/Mo/TaN/Ta/100 nm-Au substrate ( $\gamma$ ), Si/Mo/TaN/Ta/100 nm-Au/150 nm-Ga after aging at RT =  $23-26^{\circ}$ C for 30 minutes ( $\psi$ ) and after 120 minutes ( $\lambda$ ). (b) shows I-V curves obtained by LSV of Si/Mo/TaN/Ta/100 nm-Cu substrate ( $\chi$ ), Si/Mo/TaN/Ta/100 nm-Cu/Ga after aging at RT =  $23-26^{\circ}$ C for 3-hours ( $\sigma$ ).

 $\sim$ 5°C lower showed lower intensity of CuGa as compared to the CuGa<sub>2</sub> (Fig. 3) even after 6.84×10<sup>4</sup> s of aging at the end of plating. This data suggests that the increase of room temperature closer to the melting temperature of Ga accelerated its diffusion and alloy formation with copper at a faster rate (Fig. 4) than the sample that was stored at lower temperature (Fig. 3).

For a given composition of copper and gallium in the layers, the following solid state reaction can progressively form.

$$Cu + 2Ga \rightarrow CuGa_2$$
  

$$CuGa_2 + Cu \rightarrow 2CuGa$$
  

$$2CuGa_2 + 6Cu \rightarrow 4Cu_2G$$

The stochiometry of the resulting compound depends on the ratio of the concentration of both copper and gallium and the time of diffusion. Marinkovic et al.<sup>15</sup> showed that when two or three compounds are formed, the inter-diffusion co-efficient of the first compound, which is formed directly from the starting metals, is about two orders of magnitude higher than the second compound, which is formed by the reaction of the first compound with the excess of the high melting metals. Similarly, the interdiffusion coefficient of the second compound is two order magnitudes larger than the third compound, which



Figure 7. A cross-sectional SEM image (a) and x-ray spectrum (b) of electroplated  $\sim 100$  nm gallium on glass/Mo/Cu substrate after 7 days.

is formed by the reaction of the second compound with the excess of the higher melting metal and so on. However the Au-Al and Au-Sn systems are an exception and do not follow the same rule.<sup>26</sup>

The study of the Au-Ga interdiffusion and alloying during room temperature aging was also carried out to understand the activity of gallium with the different metal system. Fig. 5 shows an x-ray diffraction spectrum of ~150 nm electroplated gallium on Si/TaN/100 nm-Au substrate after aging at room temperature of 23–25°C for (a) 1200 s and (b) 7200 s. After 1200 s both the AuGa<sub>2</sub> and GaAu phases have formed and the amount of gold phases has been decreasing. However, at the end of 7200 s of aging at that room temperature, the intensity of AuGa<sub>2</sub> started to decrease and the GaAu phase plus a new gallium-gold phase GaAu<sub>2</sub> dominate in the spectrum. In addition, over these 7200 s periods the intensity of the Au (111), Au (311) and Au (222) becomes zero.



Figure 8. (a) SIMS profiles from the sample of glass/Mo/40 nm-Cu/100 nm-Ga. (b) Annular dark field image, arrow indicating the surface, corresponds to arrow in (c). (c) EDS profile taken along the line shown in (b); (d) Bright field image labeled with the compositions measured by EDS.

This data suggests that there is no un-reacted gold in the film and all the gold in the films must have been alloyed with gallium at the end of a 2-hour of self-annealing. It can be seen that the interdiffusion and phase formation of gold-gallium system was faster than the copper-gallium system. These data well agreed with previous findings in the literature<sup>15</sup> as the diffusion coefficient of Ga in Au  $(1.6 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1})$  in Au-Ga thin films is larger than the diffusion coefficient of the Ga in the Cu  $(3.1 \times 10-15 \text{ cm}^2 \text{s}^{-1})$  in Cu-Ga system at room temperature. This means that the reaction rate of gold with gallium is higher than with the copper. V. Simicand et al.<sup>16</sup> reported that the interdiffusion at room temperature leads to the formation of intermetallic binary compounds of gallium and gold. Depending on the at. wt.% of Ga and Au, composition, and the diffusion time, the different Au-Ga intermetallic compounds are formed. For a given composition, the same compounds are formed irrespective of the diffusion medium. They have shown that if Au is coupled with more than 33 wt% of Ga, then the compounds formed after 60-120 s remain unchanged for 360 days but if the wt% of Ga  $\leq$  33% then the compounds formed between 4 days to 3-months have transformed to equilibrium compounds over the period of time. Our data, however, does not quite agree with Simicand's observation. In our case, we used 30-60 wt.% Ga and observed that at first an intermediate metastable compound (CuGa<sub>2</sub> or AuGa<sub>2</sub>) is formed by the reaction of Ga with Cu and Au. These metastable compounds further react with Cu or Au and formed an equilibrium intermetallic compound (e.g. CuGa or AuGa).

LSV can be used to identify these Cu-Ga and Au-Ga intermetallic compounds. The time dependent XRD study during self-annealing of Ga-Me (Me = Cu, Au) showed that depending on the interiffusion coefficient of the Ga-Me system, the composition and diffusion time, different intermetallic compounds form. The compounds, which have been identified by XRD during aging, can be correlated with the

anodic peaks obtained by LSV. These anodic peaks would be the characteristic peaks for the particular phases or compounds which are formed during self-annealing. The anodic peaks towards the more positive potential correspond to more noble alloy compounds.

Fig. 6 show the I-V curves obtained by LSV over a potential ranging from -2V to +2V (SCE) at  $0.05Vs^{-1}$  in 0.5M NaOH. Fig 6a shows I-V curves obtained by LSV of Si/Mo/TaN/Ta/100 nm-Au substrate (y), Si/Mo/TaN/Ta/100 nm-Au/150 nm-Ga after aging at RT = 23–26°C for 1800 S  $\psi$ ) and after 7200 minutes ( $\lambda$ ). It can be seen from the I-V curve  $\gamma$  that at the potential more negative than -1.648 V and more positive than 1.182 V (vs. SCE) the current increases exponentially due to the hydrogen and oxygen evolution respectively and the peak at 1.61 V (SCE) presumably represents the oxidation of gold. In addition to these characteristics responses of I-V curve  $\gamma$ , the I-V curve  $\psi$  and  $\lambda$  shows 4 and 1 anodic peaks respectively. The anodic peaks in curve  $\psi$  at -1.09 V, -0.789 V, 0.609V and 0.927 V (SCE) are thought to be the oxidation of absorbed hydrogen on the surface, the stripping of a thin gallium films from the surface, AuGa<sub>2</sub> and AuGa intermetallic compound respectively. On the other hand, the anodic peaks in curve  $\lambda$  at 0.88 V (SCE) most likely represents the stripping of the GaAu compound. Gold is a noble metal and its oxidation can be expected at a more positive potential. However, the Me intermetallics with gallium are expected to be less noble than the gold. Depending on the composition of the stripping potential, Au<sub>2</sub>Ga is expected to be more noble than AuGa or AuGa<sub>2</sub>.

Fig 6b shows I-V curves obtained by LSV on Si/Mo/TaN/Ta/100 nm-Cu substrate ( $\chi$ ), Si/Mo/TaN/Ta/100 nm-Cu/Ga after aging at RT = 23–26°C for  $1.08 \times 10^4$  s ( $\sigma$ ). It can be seen from the I-V curve  $\chi$  that at the potential more negative than the -1.56 V (SCE) the current increases exponentially due to the hydrogen evolution. However, the peak at 0.0 and 0.78 V (SCE) is probably due to the oxidation of

Cu to Cu<sub>2</sub>O and CuO respectively. In addition to these characteristics responses of I-V curve  $\chi$ , the I-V curve  $\sigma$  shows 5 anodic peaks at -1.07 V, -0.796 V, 0.03V, 0.78V, 1.21 V (SCE) respectively assumed to be corresponding to the oxidation of hydrogen, Ga or Ga<sub>2</sub>O<sub>3</sub> stripping, oxidation of remaining Cu to Cu<sub>2</sub>O and CuO and oxidation or striping of the CuGa intermetallics.

A cross-section SEM image and x-ray spectrum of electroplated  $\sim$ 100 nm gallium on glass/Mo/Cu substrate captured after  $10.08 \times 10^4$ s at the end of electroplating are shown in Fig 7. The samples were held at room temperature (17-20°C) during the aging period. It can be seen from the XRD data that Ga readily diffuses to the Cu and Mo layers and forms CuGa, CuGa2 and GaMo3 intermetallics during selfannealing. The SEM image (Fig. 7a) shows an irregular penetration of gallium or its alloys with copper into the Mo layers. Sputtered Mo has a columnar structure and its grain boundaries normal to the substrate are considered to be a potential path for the diffusion of Ga or its alloys. As gallium and copper are lower melting point metals than Mo, their diffusion coefficients are expected to be higher and thus diffuse to the Mo very readily. However, when Ga was plated on a substrate containing a TaN barrier layer (Fig. 3) there was no Ga-Mo alloy detected even after  $5.184 \times 10^6$  s aging. Therefore, TaN acts as a diffusion barrier for gallium. Since major peaks of Mo-Ga phases overlap with the peaks of Mo and GaCu, it is hard to distinguish Mo-Ga phases in the XRD spectrum. However SIMS and chemical analysis at the nanoscale using a TEM/EDS, confirmed that the Ga diffused into the Mo.

A SIMS profile plotted with thickness (nm) vs. secondary ion intensity (c/s) of the sample (Fig. 7) shows the depth profiles of Ga, Mo and Cu (Fig. 8a). The first  $\sim$ 100 nm of the top surface is gallium rich. However, as the depth penetration progresses the concentration of Ga is rich up to  $\sim$ 50 nm inside the Mo layer and then falls off. The SIMS profile also shows that both Ga and Cu diffuse into the Mo through out entire thickness of the 600 nm Mo.

The sample was further analyzed by TEM and EDS as shown in Fig. 8b–8d. The composition, measured by EDS along the line shown by an arrow in Fig. 8b, is plotted as a function of the thickness vs. the number of counts (Fig. 8c). The first 15 nm of the profile were on the organic coating layer and thus shows no counts for Ga, Cu and Mo (Fig. 8c). Further along the profile, 25–35 nm from the surface into the Mo layers shows a high concentration of Ga. These data agree with the data obtained by SIMS. However, further along the profile, within the Mo shows only the presence of Mo which does not quite agree with the SIMS data. The discrepancy between the EDS and SIMS data could be explained by the limited sampling size of EDS compared to the SIMS. In addition, SIMS has lower detection limits. The Ga and Cu observed in the Mo layer by SIMS may be in the intergranular region and the EDS may have been done on individual Mo column.

One final explanation may be found in the image in Fig 8d. We observed islands forming on the Mo layer and these islands contained Cu while next to the island no Cu is detected, only Mo and Ga. However, why the copper accumulated in a localized bump yet has to be resolved by a further study.

#### Conclusions

The solid state reaction of electroplated Ga thin films with Me (Me = Cu, Au) have been observed during aging at room temperature. The stoichiometry of the resulting equilibrium compounds depends on the ratio of at. wt% of both Ga and Me as well as the time of diffusion. We observed that the increase of room temperature closer to the melting point of gallium (29.7°C) accelerated its diffusion and

solid state reaction with Me at a faster rate than the sample stored at lower temperature.

Our study shows that if at. wt% of Me  $\gg$  Ga, then an equilibrium compound of Me<sub>x</sub>Ga is formed where x>1. However, if at. wt% Ga>> Me then the equilibrium compound of GaMe (1:1) is formed and remaining Ga diffused into the next layer (in this case Mo). We found that TaN acts as an effective diffusion barrier layer to the gallium diffusion.

The Ga-intermetallics formed after alloying could be identified using Linear Sweep Voltammetric Stripping. The anodic stripping peak of CuGa shift towards the more positive potential (more noble) but in AuGa system the anodic peaks are shift to a negative (less noble) potential.

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