ESRF	**Experiment title:** In situ studies of graphene CVD growth on Cu-Sn liquid alloy: Atomic structure, composition, and interactions at Gr/Cu-Sn interface	**Experiment number**: MA-5338
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Report:

We performed an *in-situ* study of graphene growth *via* chemical vapor deposition (CVD) on liquid metal alloys by XRR, GID, and X-ray spectroscopy techniques. The energy of the X-ray beam was set to 22 keV. The goal of the DirectSepa project was to find a low-melting temperature metal catalyst as a replacement for high-melting temperature copper while maintaining the decent catalytic activity and the quality of the growth graphene in order to facilitate the development of technologies for the transfer of graphene directly from the liquid substrate to a solid one. Therefore, we tested the growth on three different alloy systems: Cu mixed with Sn, In, and Ga at different mass ratios. We recorded XRR and GIXD spectra on the clean liquid alloy surfaces before and after the graphene growth. We discovered that both Sn and In reveal relatively poor catalytic activity towards graphene: even with the smallest admixture of these metals (5 wt%), we could not achieve single-layer growth. On the contrary, the addition of Ga does not lead to a drastic change in the growth mechanism. By varying the growth temperature and the gas flows, we achieved single-layer growth up to 60 wt% of Ga. The corresponding XRR curves are shown in Figure 1a. The presence of only one Kiessig oscillation signifies the monolayer graphene. The growth rates drop above 60 wt% of Ga, and the growth mode changes to dendritic and 3-dimensional. This can be seen by the graphite Bragg peak around 1.8 $Å^{-1}$ on 70% and 100% Ga curves.

We used Refl1d software to fit the XRR curves. We applied a slab model containing three slabs: Cu, C, and a void in between. The void width directly corresponds to an important parameter - the interlayer graphene-copper gap [Jankowski 2021, Konovalov 2022]. The gap values obtained by fitting the XRR curves for the series of CuGa samples are shown in Figure 1b, where we can observe an apparent increase with a higher Ga percentage. This is an important result of the experimental session evidencing that we can grow a single-layer graphene at much lower temperature than on liquid Cu and that the binding force between the layer and the Ga alloy surface might be lower than that on Cu. This opens a good perspective for the development of the possible approaches of the graphene transfer to a support or a device.

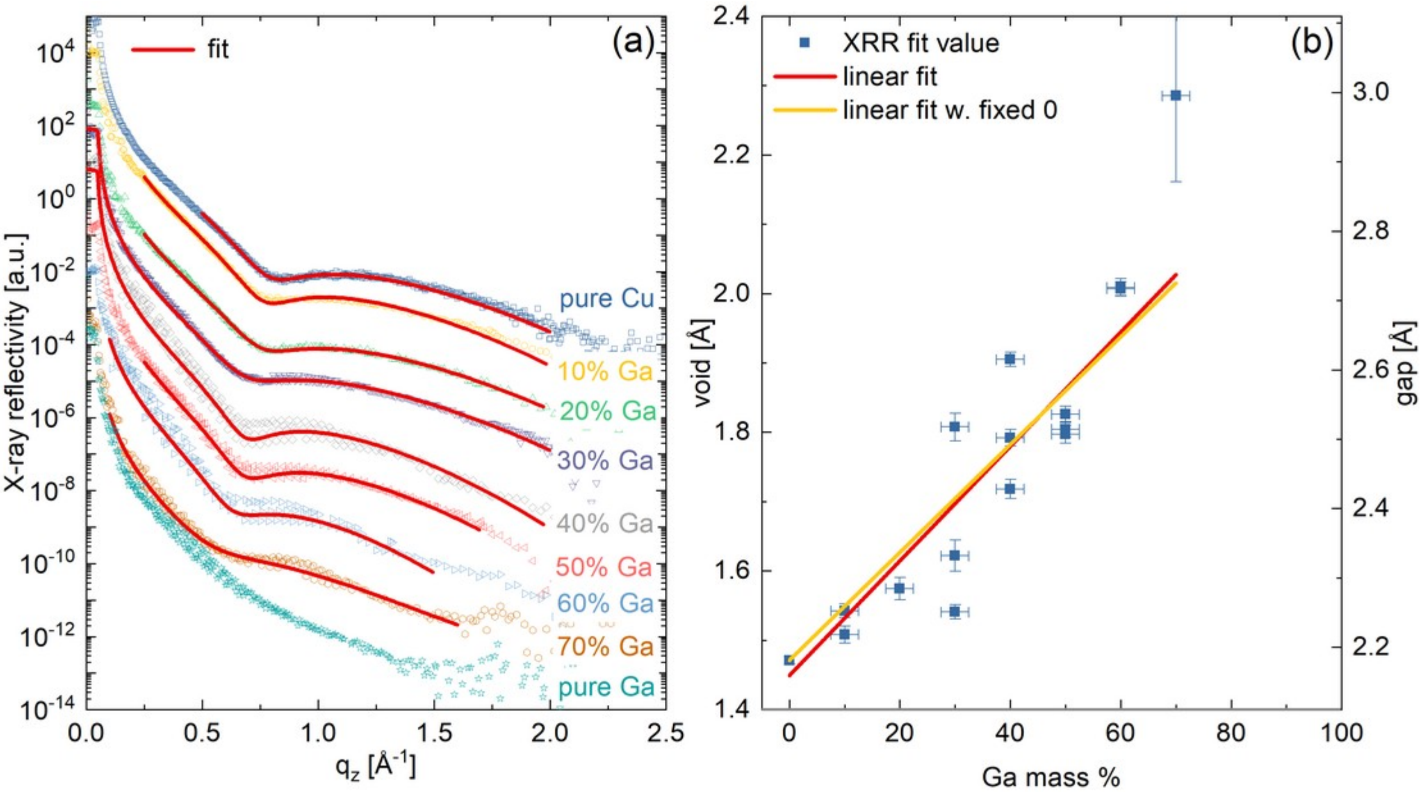

Figure 1 (a) XRR curves of the series of liquid CuGa alloy samples with CVD grown graphene/graphite on top along with the fit based on a slab model. (b) Graphene-copper interlayer gap thickness values were extracted from the fit of the XRR curves (void between Cu and C slabs plus half of the c C slab, 0.71 Å). The linear fit (red and yellow) demonstrates the linear dependence of the C-Cu gap on the content of Ga.

We also carried out an X-ray fluorescence study to probe possible surface layering of the components of the alloys and the Gu-metal mass ratio at the interface where the growth occurs. The incident angle variation did not reveal any Cu/Ga variation, possibly due to the sample surface curvature. Also, the comparison between the XRF spectra of the samples with different compositions shows that there is no significant deviation of the actual percentage from the nominal one (Figure 2). Therefore, we assume that our estimation of the composition of the alloys is trustworthy within an error bar of 5%.

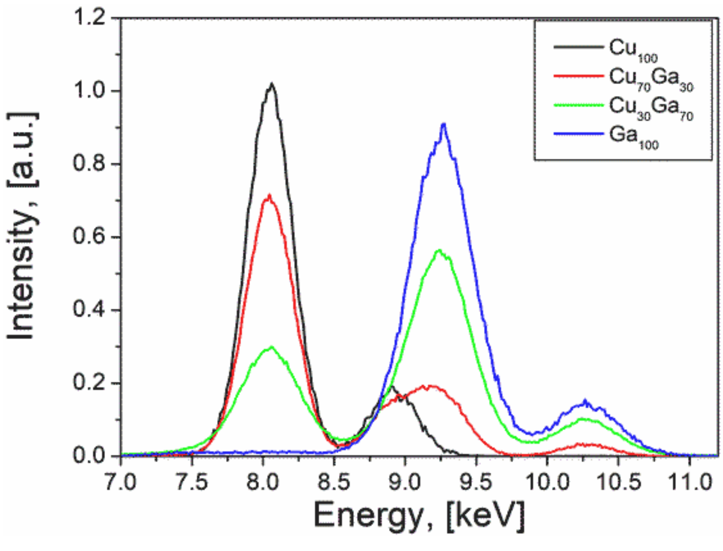

Figure 2 XRF scans of pure Cu, pure Ga, and two mixed samples.

References:

Jankowski M. *et al*. Real-Time Multiscale Monitoring and Tailoring of Graphene Growth on Liquid Copper, ACS Nano (2021), 15, 9638−9648

Konovalov O.V. *et al*. X-ray reflectivity from curved surfaces as illustrated by a graphene layer on molten copper, J. Synchrotron Rad. (2022) 29, 711–720