Response to Reviewers' Comments for

Manuscript ID materials-3009814

Dear **Editor/Referees**,

We are very grateful for the editor and referees' positive evaluation as well as the given comments and constructive suggestions, which are all considered carefully and are helpful to promote the quality of this manuscript. Here, we submit a revised version of our manuscript entitled "**Long-Term Corrosion of Eutectic Gallium, Indium, And Tin (EgainsnEGaInSn) Interfacing with Diamond**", which has been modified according to the referees' comments. All the referees' comments were answered point by point in this letter. The authors want to thank the referees for their effort and the comments and encouragement given.

Please note the main revision is highlighted in yellow in the revised Manuscript for your and the reviewers' convenience.

Referee #1:

Manuscript by Stephan Handschuh-Wang et al. reports the investigation into the long-term corrosion effects of eutectic gallium, indium, and tin (EGaInSn) interfacing with diamond surfaces. The study is notably well-structured and meticulously detailed in its approach, delivering valuable insights into the stability and compatibility of diamond coatings with liquid metals for thermal management systems. The authors have demonstrated the resistance of diamond coatings to corrosion and penetration by liquid metals over an extended period, a significant finding considering the corrosivity of liquid metals like EGaInSn towards conventional metals used in electronic devices. The study elucidates the phenomenon of liquid metal solidification due to oxidation and subsequent hydrolysis to GaOOH, a process that was verified through various analytical techniques, including SEM, EDS, and XRD.

Q1: The manuscript mentions that the diamond did not corrode nor was it penetrated by the liquid metal. Could you elaborate on whether any microstructural changes or phase transformations occurred within the diamond coating itself over the long period of exposure to EGaInSn?

Answer to Q1: The diamond coating in Figure 1b, d, and e is a structured diamond coating coming from the same batch as the sample in our previous paper: ACS Appl. Mater. Interfaces 2020, 12, 40891−40900. The SEM micrograph of the initial coating is therefore published in the mentioned article and shown below denoted with b.

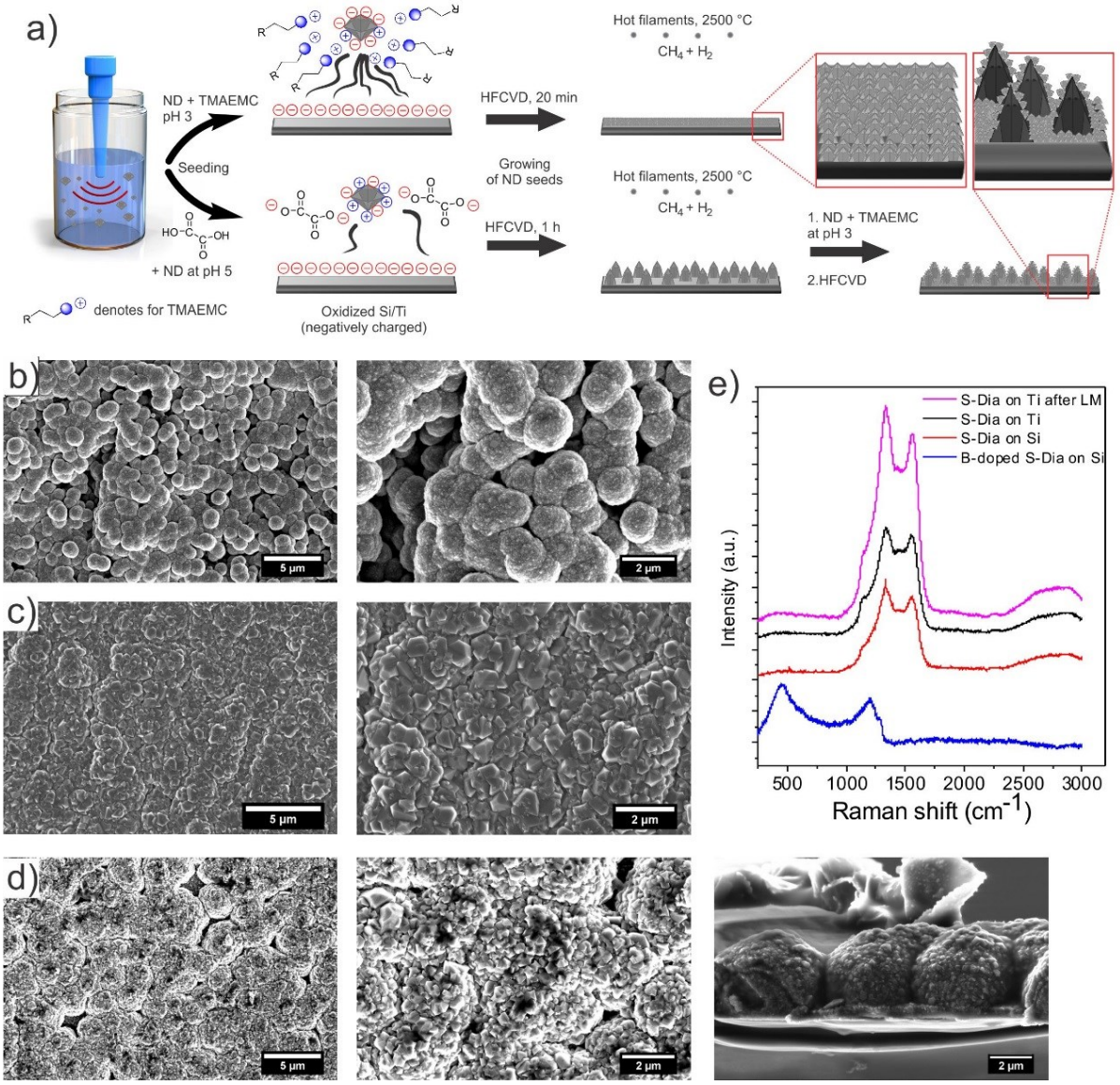

Figure R1. (a) Schematic illustration of the diamond coating process for thin unstructured and structured diamond coatings on Ti alloy. SEM micrographs of structured diamond coating on Ti (b), flat BDD deposited on Ti (c) and structured BDD deposited on Si (d). In line (d) also the cross-section of the boron doped structured diamond coating deposited on Si is shown. (e) Raman spectra of various diamond coatings deposited on Si and Ti. Here, S-Dia denotes for structured

diamond coating made via the process shown in (a). Furthermore, B-doped denotes for a BDD coating. (from: ACS Appl. Mater. Interfaces 2020, 12, 40891−40900)

One can see from the SEM micrographs that there is little change in surface morphology of the diamond coating, as the images we show in the manuscript are images after the 4 years of exposition. We agree that we should make this more noticeable in the MS. Similarly, the BDD coating we showed in Figure 1c and f is similar to the coating in Figure R1d (from the seeding process) and Figure R1c from the deposition (growth process parameters). Thus, the diamond grains grown appear similar in morphology to the latter (Figure R1c), and indeed the crystals do not show difference to this coating, even though in contact with the liquid metal for 4 years. Furthermore, the Raman spectra were also taken after the four years interfacing period (If we did this also before, we would have discarded the one sample where only graphite was deposited.). We can therefore, compare the old data (Figure R1e), with the data after contact with the liquid metal, which is shown blown up and with annotation (Figure R2). The peaks representing the diamond phase (1332.0 cm-1 or close to that) were detected in 2020 (Figure R2) and can be detected in our submission. There is no difference in peak location with Raman shift being 0.1 or 0.6 cm^{-1} close to the peaks before (Raman peak). Further, the shape of the Raman peaks is very similar and the ratio between the diamond peak and the graphite peak remains the same. Note that Raman is more sensitive to graphite than to diamond, leading to exaggeration of the graphite peak, but also to better see its change. Beside the Raman peak for the nanocrystalline diamond on Ti, the Raman peaks for the BDD coating can be compared. Indeed, the BDD coating features a similar peak shape with a peak at 1201 cm-1 and a shoulder at 1288 cm-1, denoting boron doped diamond (after contact for 4 years with liquid metal). The initial Raman spectrum of such a coating is shown in Figure R2 with a peak at 1203 cm-1 and a shoulder at 1278 cm-1. Therefore, we inferred that no change in diamond coating has occurred. Something, which occurs even without the presence of liquid metal is the oxidation of the diamond coating (surface oxidation), which could be measured with XPS. However, this occurs even without the presence of liquid metal, and quite fast (we think within a few weeks). Therefore, we did not measure this. In EDS we showed that the liquid metal does not diffuse in

the grain boundaries (likely due to room temperature). At CVD coating temperatures, diffusion of metals is known to occur though (i.e., Co diffusion during CVD diamond growth on WC-Co).

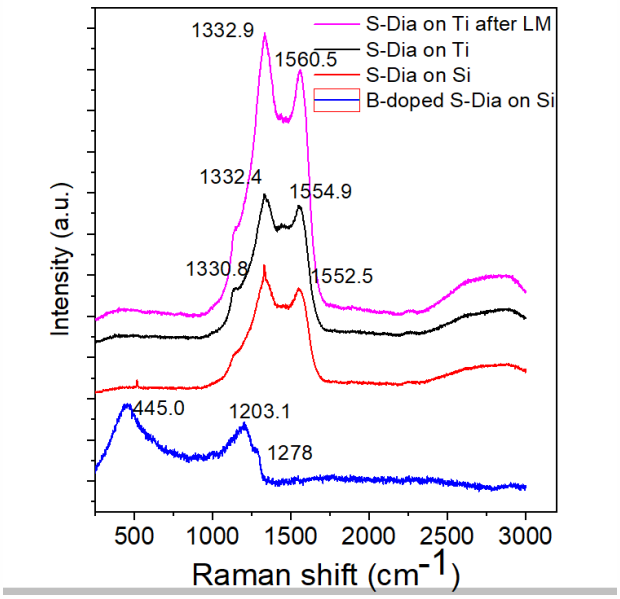

Figure R2: Raman spectra from Figure R1 annotated (taken from ACS Appl. Mater. Interfaces 2020, 12, 40891−40900)

Q2: The report outlines the hydrolysis of gallium alloys in detail. Given the significant role of environmental humidity in this process, how might varying humidity levels affect the rate and extent of liquid metal solidification and the overall stability of the system?

Answer to Q2: Indeed, this is a good question. Corrosion is dependent on the external parameters, such as temperature and humidity. Here, in south China, humidity is high in summer, and electronic device (even little used ones) will fail quickly (the only protection is to always have a de-humidifier running or an air condition on). For instance, the relatively new stereo amplifier (of one of the authors) just broke down after only 3 years of sporadic use, the technician quoting excessive corrosion on the inside. We believe that the amount of salt in the air (as we are located near the ocean) exacerbates the corrosion.

Circling back to the question. The hydrolysis should be investigated in detail with humidity control at different temperatures (and humidity). We are quite certain that there is an onset humidity where hydrolysis is observed. We do not know at which value is (currently). Quantitative measurement of this is still a bit of a problem, but we are working on this. We mention now in the manuscript that hydrolysis speed depends on temperature and humidity (presumably).

Q3: In your experimental setup, was there any consideration or measurement of mechanical stresses that might have arisen due to the differing thermal expansion coefficients of the metal substrate and the diamond coating, particularly under temperature variations?

Answer to Q3: The experiments with the liquid metal were conducted at room temperature (as we do not have access to an oven that can be heated to 200 °C or more for an extended period of time) Thermal stresses in the diamond coating originate from the CVD growth during coating fabrication, and as can be seen from the Raman measurements, the stresses remain in the coating during the 4 years. Mechanical stresses for diamond are generally measured with Raman spectra using the peak shift method, which we cited in the manuscript. In principle, these stresses can also be calculated, but calculated ones do not account for the intrinsic stresses. Note that the stresses (by Raman) are average stresses, stress is different for the initial growth, and later growth processes (increase in thickness of the coating). Further, stress constitute thermal stress and intrinsic stresses. (see: 10.1016/j.diamond.2016.12.008)

I recommend this manuscript for publication in your *materials*. However, addressing the above questions should be completed before considering it for publication.

Referee 2:

The work needs to be corrected in several aspects as described below.

Q1: The authors wrote: 'The diamond coatings were either flat (smooth, Figure 1a, later discovered to be graphite)' (see lines 178-179). Although in the discussion of Figure 1a, there is

a note about the later discovery that the coating was graphite, but the clarification of this discovery process should be added to the text.

Answer to Q1: We assumed at first that all coatings were diamond. However, this one coating was not diamond rather graphite or diamond like carbon on Si. However, we did not measure Raman or SEM prior to the interfacing with the liquid metal, but only after the fact. The graphite on the surface was later detected by Raman (and the SEM image also signifying this). We considered at first removing this image, but opted for showing this, as even though it was graphite it also impeded the diffusion of the liquid metal (albeit the graphite is not expected to be mechanically strong, i.e., low wear resistance).

Q2: The authors wrote" "The structure is consistent with the one published previously.28" (see lines 185-186). Although the text mentions that the structure is consistent with previously published work (reference 28), in my opinion authors should briefly summarise the key findings of that work to provide context.

Answer to Q2: Thanks for this comment. We added that the sphere size of the diamond coating features a similar size and that a similar multilayer is observed and the context of the previous article was briefly explained.

Q3: In my opinion, authors should add more explanation between the experimental observations and the hypotheses in Section 3.2., especially of the liquid metal solidification process, referencing similar phenomena in other studies for comparison. Moreover, the hypothesis of aluminium dissolution should be discussed with more references to the existing literature on gallium alloy interactions with various metals.

Answer to Q3: We did not find any publication discussing the drying of liquid metal in air, but in contact with copper in bearings. These we now mention, together with a brief information of corrosion of aluminum:

"It is known that gallium corrodes aluminum and aluminum alloys (albeit aluminum has limited solubility in gallium).[1] This corrosion commences via the diffusion of gallium into the grain boundaries, and dissolution of aluminum.[1a] This corrosion is an issue for aluminum heat sinks in contact with gallium, but is useful for hydrogen production via the reaction of aluminum with water, where gallium activates the aluminum.[1a] Further, dissolved aluminum oxidizes on the liquid metal surface, resulting in a dark grey to black oxide on the surface. Therefore, an assumption was that alloying with aluminum from the Ti-alloy lead to the solidification of the liquid metal. Disappearing (likely drying) presumably due to alloying was observed previously[2] for liquid metal bearings (gallium alloy in contact with copper). Contradicting this hypothesis, the liquid metal also solidified on the diamond coatings on Si, as no metal for alloying is available on the Si-coated samples."

We also have an article showing the experiment of dissolution of aluminum, followed by the reaction of it with water (Al-Ga amalgam with water, 10.1002/ckon.202300041). However, we did not add this in the article due to comment 8 of the referee.

Q4: The information presented in lines 238-246 should be described in more detail. The authors should clarify the timeline of observations and the transition from liquid to solidified states of the liquid metal, as well as expand on the reasons why the initial hypothesis about aluminium dissolution was ruled out.

Answer to Q4: As stated in the manuscripts, the samples were only observed sporadically. As there was no change in the first year, we, at first, thought that the experiment was a failure and did not assign a high priority to the experiment.

We saw that three of the samples solidified, and one of these solidified liquid metal samples was deposited on diamond coated Ti, one was deposited on pure Ti (the other liquid metal on Ti-alloy sample) did not show this effect. Similarly, one diamond coated Si sample showed this. In hindsight, we assume that this is an effect of amount of liquid metal on the sample and how

much oxygen was introduced into the liquid metal by the forced wetting method, rather than an effect of the substrate. As we agree that the sequence of the solidifaction should be given in the MS, as it might give some hidden information, we added the following sentence:

“After storage for two years, the liquid metal on three samples became sluggish, namely, sample 3 (one of the two rough diamond on Ti samples), sample 4 (one of the two bare Ti samples), and sample 8 (one of the rough BDD on Si samples), while the other samples remained liquid”

Q5: In Section 3.3 authors explained the solidification process and the role of hydrolysis and dealloying, however, additional context on the relevance of these findings to broader applications, such as in thermal interface materials and electronics, would enhance the discussion.

Answer to Q5: Liquid metals are not only used in electronics and thermal interface materials, but in catalysis, biomedicine, seals, bearings (liquid metal bearings for CT), thermometers, barometers, blood pressure measurement and so on (or are anticipated for these applications). In most of these applications. In all these applications, the hydrolysis poses problems with storage and performance. (see next question for some solutions in industry). For biomedical applications, hydrolysis poses a problem for storage of liquid metal nanodroplets and liquid metal enabled stretchable electronics (i.e., for stretchable electrodes). Especially, when using liquid metal micro- or nanodroplets in the synthesis.

We added the following sentences: “Similarly, the hydrolysis is also a challenge for other applications, such as stretchable electronics (especially, miniaturized electronics), as the electrical conductivity is far lower than that of the liquid metal,[4a] and could lead to discontinuity due to its brittle and pow-dery nature (see Figure 4a).

Q6: The authors should add a discussion, based on the results obtained, about potential strategies to mitigate the hydrolysis and dealloying effects in practical applications.

Answer to Q6: Avoiding hydrolysis is difficult in humid environments. There have been a couple of useful methods. The first is using inert atmosphere, as it has been done for Galinstan thermometers, or is done for surface tension measurements of liquid metals. This avoids not only hydrolysis but also oxidation. A second method is the use of antioxidants, which has been done for blood pressure devices.[3] For commercial liquid metal bearings, the use of several bearings has been proposed, see for instance patent US11020067B1. Another method is limiting the humidity the device is exposed to by a de-humidifier, which may be difficult for a portable device. In research literature, the hydrolysis was not mentioned as a problem, and thus there are little suggestions on how to deal with it for gallium alloys. Other metals are greased, perhaps, greasing the surface of liquid metals could be a solution in conjunction with several seals? But this is at this point only an assumption. As far as we know, there has not been a solution to this issue in the thermal interface community (see PlayStation 5 and the associated issues with “dry” liquid metal).

Q7: The conclusion section should be expanded. For example, while the process of oxidation and hydrolysis leading to the formation of GaOOH and dealloying is mentioned, more details on how these findings affect practical applications should be included. Furthermore, the authors should discuss the broader implications for the use of liquid metals in various technologies and the importance of developing protective measures.

Answer to Q7: We also think that this hydrolysis in air (at higher humidity) poses a problem for widespread use. Specifically, for high humidity regions (tropical regions). However, in the conclusion paragraph, we cannot get in too much detail on this. We added the following sentences in the MS to accommodate the comment:

“These processes affect applications ranging from thermal interface materials, stretchable electronics, slip rings, and switches via catalysis and solvents to biomedical applications of liquid metals based on liquid metals and is exacerbated at high temperature, high humidity, and small liquid metal entity size.”

Q8: 8 references by one author (Stephan Handschuh-Wang) is a lot for 54 references (above 14%). The authors should minimize this or justify the need for citation.

Answer to Q8: In general, 20 % self-citations is considered ok, but we can explain the relevance of the reference in detail. The median self-citation value was found by a research group to be near to 12.7 %. https://journals.plos.org/plosbiology/article?id=10.1371/journal.pbio.3000384, As we added a few references, we are likely now below this percentage. (btw. I recently reviewed an article with 100 references, where 98 were from the authors; I stated this in my review and the article was published without any changes…)

The Journal of Physical Chemistry C **2021**, 125, 20113, gives important values for surface tension, thermal conductivity, and electrical conductivity, is cited several times in the article, as it also shows the difference in thermal conductivity between gallium, Galinstan and gallium oxide. (also gives melting temperatures.

Materialia **2022**, 26, 101642, This reference is important as it gives the specific melting temperature and composition (disambiguous to Galinstan®). Galinstan and Galinstan® are often confused in scientific terminology and papers. Here, also a reference EDS spectrum is available, which was used to discern the differences, between aged and not-aged sample of liquid metal.

ACS Applied Materials & Interfaces **2020**, 12, 40891. This is the article, where similar samples have been made the first time. We use it to compare with the ones in this article.

https://doi.org/10.1002/adfm.2023134742313474; this article was made with a similar rough diamond coating in contact with liquid metal. This and the previous article are the origin of this article.

ACS Applied Materials & Interfaces **2020**, 12, 24432. The first time, the structure we discuss in this article was published. Therefore, we have to cite this reference.

Applied Materials Today **2020**, 21, 100868. This review article discusses wetting and adhesion, as we use forced wetting, we should cite the article to show how this works. There was just a few days ago another article published by Dickey and others, but the article does not yield new information, thus, I like to cite the older one. The wetting and adhesion of liquid metals on the metallophobic samples (diamond) was also shown in our previous article in materials: *Materials* **2020**, 13, 2283. Therefore, we used this reference.

Langmuir **2022**, 38, 14475. The Langmuir article discusses hydrolysis of liquid metal in water and at the air water interface. It also shows XRD results and is thus a valuable reference for this article.

Q9: The authors should standardize the work in terms of the style of the manuscript. For example, in many places there is an incorrect font.

Answer to Q9: We apologize for this. We have checked the manuscript once again and now it should be all homogeneous.

[1] a) S. Jang, S. M. N. Jeghan, E. Seon, Y. Tak, M. Kim, G. Lee, *International Journal of Hydrogen Energy* **2023**, 48, 13390; b) Y.-G. Deng, J. Liu, *Applied Physics A* **2009**, 95, 907.

[2] a) D. Bagchi, J. Raj, A. K. Singh, A. Cherevotan, S. Roy, K. S. Manoj, C. P. Vinod, S. C. Peter, *Advanced Materials* **2022**, 34, 2109426; b) S. Liu, D. Qu, S. McDonald, Q. Gu, S. Matsumura, K. Nogita, *Journal of Alloys and Compounds* **2020**, 826, 154221.

[3] a) R. Kumar, M. Kumar, G. S. Wander, A. K. Sahani, *Scientific Reports* **2022**, 12, 15813; b) L. T. Taylor, J. Rancourt *Patent US5792236A*, **1998**.