REPORT1

Weaknesses

1. Systems Au-C and K-C are not suited for comparison with TRIDYN →We addressed this by moving the TRIDYN simulations of the Au–C and K–C systems to the appendix, while in the main text mentioning the immiscibility as a cause for the disagreement of TRIDYN and the experimental results. While TRIDYN is indeed not suitable for such systems, we believe that illustrating where the model fails is scientifically valuable—especially for the nuclear physics community, which may not always be aware of its chemical limitations. This clarification has been incorporated into the revised manuscript.

2. Experiments suffer from sever oxygen contamination → Thank you for pointing out the significance of the observed oxygen content in the experimental data. TRIDYN simulations for oxide materials (Al_2O_3 and ZnO) were already included in the initial version of the manuscript. We have further clarified this description by adding the specific implantation scheme

3. oxygen is not included in the TRIDYN simulations → For the K-on-C implantation case, we had already performed additional TRIDYN simulations including oxygen. However, this did not improve the agreement with experimental data, likely due to the limitations of TRIDYN in these immiscible cases. This has now been added in the manuscript (line 208).

4. RBS should be carfully analyzed and also simulated properly → The RBS spectra were simulated using SIMNRA, as noted in the original submission. This now appears explicitely in the revised version (line 75).

5. Title may be misleading → We agree with that the original title may imply a broader or more conclusive validation of TRIDYN than the data supports. To clarify the scope, we have modified the title to:
"Experimental evaluation of self-sputtering yields and comparison with TRIDYN simulations."

Report

Referee report on submitted manuscript
Experimental validation of TRIDYN self-sputtering simulations
By
M. Heines and M. Deseyn, B. Caerts, T.E. Cocolios, R. Heller, U. Kentsch, G. Magchiels, W. Möller, L. M. C. Pereira, A. Vantomme, W. Wojtaczka and Q. Zhao

The authors describe a comparison of the retained amount of implanted materials after high fluence implantation into (basically) elemental targets between experiment and TRIDYN Simulations.

The experimental conditions, in particular ion energies ion fluences etc. are incomplete and should be compiled in a table. This should also include the vacuum conditions to evaluate the possible incorporation of Oxygen. It is also important in how many steps the implantations were done, inbetween the samples were extracted to ambient conditions.

→ A table was added containing the vacuum, current density and implantation energy as well as a table in the appendices that includes the different implantation steps with the corresponding ion fluences. It is our belief that those frequent exposures to air are the reason for the oxygen contamination, rather than the vacuum condition of the implantation.

For implantations of K and Au into glassy carbon it is relevant to consider the binary phase diagrams.
C-Au is essentially immissible and Au may form clusters and/or preferentially diffuse to the surface. It is known that ion irradiation of Au in Si leads to a Au surface layer due to diffusion.
C-K is also mainly immisible, although a potassium carbide exists, however this carbide is a specials ionic bonded compound with triple bonded C dimers.
Therefore, the system Au-C and K-C will behave in a very special way due to their phase diagrams. TRIDYN as well as any other BCA Monte Carlo program do NOT account for such an immisible behavior. It is therefore not surprising that the simulations and the experiments show a largely different behavior.

As a conclusions, BCA simulations are not able to predict the self-sputtering yields in those immissible binary systems. They can predict the situation on a very short time scale of a duration of a collision cascade. Any off effects are thermodynamic effects and diffusion behavior which is beyond the scope of the BCA simulations.

→This is now mentioned in the article and the experimental results have been moved towards the appendices to avoid cluttering the message of the main manuscript.

Implantation of Yb into Al and Zn is quite different because both binary systems possess a complex phase diagram with many thermodynamically stable phases. Therefore, implanted Yb will be chemically bound in Al as well as Zn and the BCA simulation will most likely reflect the correct local stoichiometry as function of ion fluence. It is then expected that the BCA simulations predict the correct self-sputtering yields and also the retained fluence.

The experiments however show a significant contribution of Oxygen and the experimental retained fluence corresponds to implantation into Al2O3 or ZnO.
Surprisingly there is also lot of Oxygen seen in the RBS spectrum after K implantation into glassy carbon.
From the intensities of the surface near O and K peak and correcting for the ration of atomic numbers (squared) the stoichiometry is roughly K_1 O_3.5, very strange, since the stable compound would be K2O.
This suggests that possible the incorporation of Water is also involved.
It ist therefore important to describe in detail the implantation conditions, including the vacuum in the implantation chamber.

→ We acknowledge the observation regarding the unexpected high oxygen content. While this indeed raises questions, such as the possible involvement of water or other contamination sources, a detailed investigation into the chemical origin of the oxygen signal lies beyond the scope and expertise of the current study, which is aimed at a nuclear physics audience. Words of caution regarding the presence of oxygen in the system have been introduced in the manuscript.

The sublimation enthalpy of C is 7.4 eV (derived from thermodynamics). The value of 4.5 eV

mentioned in ref [13] comes from an adjustment of the BCA simulations to match the experimental sputter yield of carbon. Since it is energetically favorable to also sputter carbon dimers (which is not taken into account by most BCA simulations), the experimental sputter yield can be explained by a lower surface binding energy than the 7.4 eV value. The assumption of 4.5 eV is therefore justified for a comparison with experimental sputter yield data.

TRIDYN suggest to use the surface binding energy matrix given in equation (1). To justify such a matrix would assume a chemically bonded binary liquid. This is fulfilled for e.g. the B-Si, B-C systems. For Si-N it would be valid upt to the Si3N4 stoichiometry, For Si-O up to SiO2 stoichiometry. The assumption is not valid for immiscible systems such as Au-C or K-C. Therefore, one should use surface binding energies based on the elemental sublimation enthalpies. Moreover, the validity of a BCA simulation to describe immiscible systems can be put into question.

→ This is now mentioned in the manuscript and the data was moved towards the appendices.

The sputter yield for ion irradiation of Ta2O5 has been studied in detail in the literature. This system is characterized by a strong compound formation enthalpy of about 21eV per molecule or about 3 eV per atom. Calculating the surface binding energies for Ta and O from eq. (2) would lead to rather high values and thus a very low sputter yield. The experimental sputter yields, however, suggest that essentially the elemental sublimation enthalpies play a role. Of course, one can use the model suggested in the TRIDYN manual but to my opinion it is not validated by experimental data.

One remark to the RBS spectrum.

The implantations were done with 40 keV and/or 90 keV ion energy, resulting in ion ranges of about 30-40 nm. This is quite narrow compared to the depth resolution of RBS at 1.57 MeV He ion energy. In Fig. 6 the non-broadened K profile is most likely the peak above 1 MeV backscattering energy. Everything else could be due to diffusion or recoil implantation. In addition, the huge signal from oxygen is surprising. I would recommend to simulate the RBS spectrum with SIMNRA in order to extract the stoichiometry in the surface near region and in larger depth of the sample.

→ The spectrum was simulated with SIMNRA, but this did not yield satisfying results.

In high fluence or high current implantation the thermal load on the target may become relevant. It is therefore important to estimate the possible temperature of the target during implantation. Even if the sample holder is cooled, the surface temperature may be high enough to allow diffusion of the implanted species, either into the bulk or to the surface.

→ The thermal load on the target was estimated using the current density of 0.077 μA/cm^2, corresponding to a power of approximately 5 mW/cm^2. This is below the threshold at which significant temperature-induced effects are expected, which typically require current densities in the order of tens of μA/cm^2. We therefore consider temperature effects to be negligible in our implantation conditions.

The manuscript should at least undergo major revisions regarding

- The immiscible system Au-C and K-C → Is now mentioned in our report and the data was moved towards the appendices
- A detailed discussion of the high oxygen content of the samples
- A quantitative analysis of the RBS spectrums
- Correct TRIDYN simulations including O as additional projectile

→ Since these data were moved to the appendix and the manuscript clearly states that immiscibility is the main reason for TRIDYN's failure in these systems, we opted not to expand the modeling scope further. Additionally, simulations with oxygen as a co-implanting species did not improve agreement with experiment, supporting this decision.
We also emphasize that this study is intended for a nuclear physics audience, and the inclusion of complex chemical systems lies beyond our intended scope.

May be the title is misleading, since it implies that TRIDYN self sputter yields were tested by experiments. As a consequence the reader may think that TRIDYN will give wrong results.
If however, the systems chosen (like Au C or K-C and an unkown source of oxygen) are not suited to predict correct self sputter yields with TRIDYN, then a comparison or validation is not possible. TRIDYN dos not give correct results if the chemistry (immiscibility) comes into play. TRIDYN may include oxygen depositions as additional projectiles to get closer to the "dirty" experimental situation, but this has not been included in the simulations.

A suitable title could be " Experimental evaluation of self-sputtering yields, comparison with TRIDYN simulations, and the role of contaminants and thermodynamics "

→The title has been adapted to reflect its message and the content of the main body of the manuscript.

I think the journals publication criteria are not met.
In the present state I cannot recomment transfer to another publication

REPORT2

Weaknesses

1. Phase diagrams of the sample system and chemistry were probably not taken into consideration -> TRIDYN mainly only suitable for homogeneous mixtures
   → We agree that TRIDYN, assumes a homogeneous target and is not suited to describe immiscible systems. This limitation is now explicitly discussed in the manuscript for K-C and Au-C, and these systems were moved to the appendix to clarify that they serve more as illustrations of TRIDYN's boundaries rather than full validation cases. The main analysis and conclusions focus on systems (e.g., Yb in Al and Zn) where TRIDYN's assumptions are more likely to hold.

2. Experiments partly with very few data points (Au-C case)
   → We acknowledge the limited data points, this is mainly because the Au-C case was the first time the self-sputtering effects were observed within the collaboration and those implantations were therefore not dedicated to understanding the self-sputtering effects

3. Implantations and experiments could be described in more detail
   → In response to both reviewers' requests, we have expanded the experimental section. We now included a detailed table of implantation parameters (ion energy, current density, vacuum) and a table showing the different implantation steps).

Report

Experimental validation of TRIDYN self-sputtering simulations By M. Heines and M. Deseyn, B. Caerts, T.E. Cocolios, R. Heller, U. Kentsch, G. Magchiels, W. Möller, L. M. C. Pereira, A. Vantomme, W. Wojtaczka and Q. Zhao

In this paper, the accuracy of tridyn simulations for ion implantations is investigated and compared with experiments. In particular, the retained fluence, measured with RBS, should provide information on the self-sputtering yield.

General Remarks:

The experiments should be described in more detail. This should include which conditions were present. Important would be the vacuum during implantation, how many implantation steps were undertaken, what exactly was done with the sample between implantations and what current was used during implantation. In addition, an estimate of the sample temperature would be helpful in order to address temperature effects.

→ A table was added with those parameters and the thermal load on the target was estimated using the current density of 0.077 μA/cm^2, corresponding to a power of approximately 5 mW/cm^2. This is below the threshold at which significant temperature-induced effects are expected, which typically require current densities in the order of tens of μA/cm^2. We therefore consider temperature effects to be negligible in our implantation conditions.

The sample systems should be examined for their miscibility and chemical bonds (e.g. whether molecules can form with the correct stoichiometry). The Au-C system in particular has a strong tendency to segregate (very low C solubility in Au (see. Okamoto, H., Massalski, T.B. The Au-C (Gold-Carbon) system. Bulletin of Alloy Phase Diagrams 5, 378–379 (1984).

https://doi.org/10.1007/BF02872953)) and therefore homogeneity after implantation, as assumed in Tridyn, cannot be assumed.

→ We have revised the manuscript to emphasize the immiscible nature of the Au-C and K-C systems. These examples are retained in the appendix to demonstrate TRIDYN's limitations in real experimental contexts and are now clearly separated from the main validation case.

Special Remarks:

Line 86-89: I question whether adjusting the surface binding energy as a fitting parameter solves the problem that gold is unlikely to mix with the carbon and move to and from the surface by diffusion. Eq. 4: Is the surface binding enrrgy here simply a fitting parameter or is it determined by thermodynamic/physical parameters? Please clearify

→ In line 88 of the new manuscript, it is mentioned that those values are taken from table 1, which contains experimental values. So, no, these are not fitting parameters.

Line 92: Can the porosity be achieved by adjusting the density in the simulation? Or can vancancies be inserted as described in [8]?

We decided not to explore this aspect as it would only provide marginal improvements which are not necessary for the application we are seeking.

Figure 1: The retained fluence is nearly the same for all energies and independent of the incoming fluence which indicates a problem with the sample system and not an error in the simulation. Since gold and carbon tend to segregate, this is not really surprising, as gold is not firmly bound in the material. The match at the low energy is probably a random result. It would be nice to see how the other energies behave at low inc. fluences and whether it then also coincidentally agrees with the simulation.

→ We thank the reviewer for the observation. While the similarity in retained fluence across energies may reflect underlying material behavior such as segregation, we consider a deeper interpretation of this trend to be beyond the scope of the present study, which is focused on evaluating TRIDYN's performance within the limitations of its model assumptions.

Line 147: To suggest the K enters deeper due to thermal diffusion, it would be nice to now the temperature during implantation.

→ No temperature readout during the implantations was available, though the ion current density during implantation was ~0.077 μA/cm^2, corresponding to a power deposition of approximately 5 mW/cm^2. At this level, no significant temperature rise is expected, and diffusion effects are unlikely.

Line 152: Is there a measurement of the oxygen between the implantation steps to see exactly when it gets into the sample?

→ Unfortunately, no direct measurement of surface oxygen content was performed between implantation steps. However, we have clarified the implantation scheme and vacuum conditions.

Conclusion: 1. The Au-C study ist not mentioned, why?

→ The Au–C case is now placed in the appendix as an example of TRIDYN's limitations due to immiscibility. We clarified its role as a boundary-case illustration rather than a validation

example.

2. The question remainds, if TRIDYN and other BCA simulations are still a good approach or whether it is just a stroke of luck if they work properly. Since 2 out of 4 implantations could not be simulated well in this work. Or do the sample systems simply need to be examined more closely before that the use of TRIDYN or BCA can be considered sensible?

→ This is a fair and important question. We do not claim TRIDYN provides universally accurate predictions, but rather aim to show its applicability within nuclear physics applications. Our results show that in chemically compatible systems (e.g., Yb in Al or Zn), TRIDYN performs reasonably well in predicting retained fluence. Conversely, in systems with chemical segregation or contamination (e.g., Au–C, K–C), deviations arise as expected. The value of this study lies in clearly identifying such boundaries for the nuclear physics community, where TRIDYN remains widely used.

In the present state I cannot recomment the paper for publication