Diamond, Thin Hard Films and Related Materials Focus Area

Objective: Conversion of hexagonal to cubic boron nitride by ion irradiation

Conversion of soft hBN into a hard cBN nanoparticle layer by light (M<15) ion implantation (Dr R. Machaka for M.Sc and D. E. Aradi for Ph.D) was reported earlier, based on Raman, X-ray and electron microscopy, and enabling the production conditions to be partially optimised. Dr Aradi continued working at Huddersfield University, and moved to a post at Manchester University in 2021 from where she continues to collaborate with DiHard. The question of whether this effect could lead to a measurable surface hardness increase which could be detected in an engineering context, using conventional Vickers indentation testing, was clearly of importance for possible applications. Mr. Lisema established the effect and its temperature parameters for his MSc which was awarded in 2019, and publications were reported previously. He is now working for a PhD on the production and implantation of BN nanotubes, an exciting area which has not received as much attention as one might expect. His work in 2020 was of course severely disrupted by the COVID-19 lockdowns, but he has set up a prototype nanotube synthesis line using ammonia gas (with assistance from the School of Chemistry) and carried out some electron microscopy on the resulting nanostructures. D. Morgan Madhuku of iThemba LABS (Gauteng) is co-supervising as before. (T.E. Derry, L.I. Lisema, E. Aradi, R. Machaka (CSIR) and M. Madhuku)

Objective: Ion implantation doping of carbon nanospheres

Studies of the possible doping of solid carbon nanospheres by ion implantation, and the electrical effects, have been resurrected by the return of Chemistry PhD Boitumelo Matsoso (working with Profs. Derry and Coville) as postdoctoral work. Solid nanosphere powder of about 2 nm size was fabricated in the School of Chemistry and implanted at iThemba LABS (Gauteng) using the unique powder implantation equipment on the Ion Implanter. Some samples were already left over from the previous work in which Dr Matsoso and undergraduate project students had participated, and she used both sample sets.

The first experiments used implantation with B^+ and N^+ ions, which were the most likely to produce positive results, plus Ne^+ as an inert control. The very large specific surface area of these nanosphere particles requires long implantation times, but sufficient modification to be visible easily in enhanced conductivity and magnetic measurements, using the Physical Properties Measurement System (Dr D. Wamwangi) was achieved. Electron microscopy and Raman spectroscopy shed light on the structural changes. Dr Matsoso has been collating results and drafting a journal paper. In April 2020, an abstract had already sent to the ICACS (Atomic Collisions in Solids) Conference in Finland, planned for June 2020, but the coronavirus led to its cancellation. (T.E. Derry, B. J. Matsoso, R.M. Erasmus, D. Wamwangi and N.J. Coville)

Objective: Raman spectroscopy in studies of residual stress and fatigue processes in polycrystalline diamond

The project continues the investigation of fatigue fracture in polycrystalline diamond (PCD) based tools using a ball-on-three-balls fatigue set-up, where samples are subjected to cyclic stressing followed by mapping with Raman spectroscopy to determine the average surface stress in the PCD layer. As indicated in the 2019 report, there were various extended delays associated with sample quality (rectified after discussions with Element Six) and equipment breakdowns at Mintek, where the hydraulically actuated fatigue instrument developed an oil leak that needed repair. The oil leak made it impossible for the hardware to properly follow the loading cycle profile programmed into the software, leading to highly premature fracture of samples. The use of their electrically actuated fatigue instrument was investigated, but the maximum cycling rate of 1 Hz was too low to make the experiments feasible. The hydraulic repair took some time so that useful experiments only took place late in 2019. Follow-up work was undertaken early in 2020, but the COVID-19 pandemic brought all research to a halt. Wits University opened for PG students from July/August 2020, but Mintek remained closed to all visitors until late 2020. The only other regional facility that can do temperature dependent fatigue testing is located at the Mechanical Laboratory at the CSIR. They were also not accessible to visitors during the latter part of 2020. (M. Vhareta, R.M. Erasmus and J.D. Comins)

Objective: To study the luminescence properties of diamond

In the 2019 report, it was indicated that after placing his PhD registration in abeyance for a while due to increased responsibilities and travel commitments after a promotion at work (which is with De Beers Technical Services in Johannesburg), discussions were undertaken with Mr Viranna in the last months of 2019 with the intention of formally continuing the work in 2020. After some preparatory work in early 2020, and before the PhD registration was taken up again, the project was placed on hold due to the onset of the COVID-19 pandemic. In November 2020, the project was taken up again, but as 7-10 days of contiguous measurement time is needed for the required PL mapping, this could not be done due to the high demand on the instrumentation by many PG students trying to complete experimental work before the end of 2020. There have been a few problems with the primary laser's cooling water flow interlock electronics. A replacement unit has been bought and delivered so this problem is solved. It is planned to continue the research from March/April 2021. N. Viranna is registered for the PhD degree part-time. (N. Viranna, J.D. Comins and R.M. Erasmus)

Objective: Thermoelectric properties of chalcogenide and intermetallic half heusler alloys for low and high temperature applications

This work follows up on the baseline work carried out by Ms. Mmapula Baloi on the determination of the minimum lattice thermal conductivity of chalcogenide of GeTe and $Ge_2Sb_2Te_5$ thin films. In 2020, the manuscript from this work was accepted by the *J. Applied Physics* subject to reviewer recommendations. The work was continued and the deposition of GeSb and SnSe thin films and implantation of Fe for spin Seebeck effects was done. So far, Ms. Mmapula has measured the magnetisation behaviour at various temperature ranges and their hysteresis behaviour has been studied. A collaboration with Dr M. Molepo has been established to provide support on the determination of the thermoelectric properties of half-Heusler alloys that will also be measured by the PPMS. On the measurement of the thermoelectric properties of chalcogenide alloys, the samples continue to optimised to be within the measurement range of the PPMS instrument. and this is currently ongoing. **(**M. Baloi, M. Molepo and D. Wamwangi)

Objective: Elastic and thermal properties of Sb_2Te_3 and $GeSb_4Te_7$

Sb_2Te_3 and $Ge_1Sb_4Te_7$ are chalcogenide alloys that lie on the "pseudo-binary" tie-line in the Ge-Sb-Te system. As such, they have stable crystalline phases that can be converted into disordered states using a laser or a current pulse. This forms the basis of universal non-volatile memory. The project forms part of the global objective to predict the nature of the acoustic phonon modes and their softening during the storage process. The dynamics of surface acoustic modes of a Sb_2Te_3-rich alloy is being investigated using surface Brillouin scattering. The project has investigated the role of the Sb-Te bonds on the elastic and thermal properties of these alloys as case studies. This project is in its final phase after having determined the elastic properties of Sb_2Te_3 and $Ge_1Sb_4Te_7$. Using acoustic wave propagation, the elastic properties of base binary phase change alloy of Sb_2Te_3 and a more Sb_2Te_3-rich $Ge_1Sb_4Te_7$ were determined for the disordered and ordered structural phases. Additionally, using Cahill's model, the minimum lattice thermal conductivity was determined for comparison with the measurements using TDTR by Dr. S. Reparaz. The determination of the elastic properties together with the longitudinal and transverse velocities of acoustic phonons has since been carried out for both phases. Coupled to these measurements were atomic densities from Rutherford Backscattering Spectroscopy. The delay in registration by the candidate has precluded supervision and thus minimised the pace of progress in this project. It is expected that the MSc dissertation will be submitted by mid 2021. Coupled to this project was the honours project on the In_3SbTe_2 by Mr. K. Singh, which sought to determine the minimum

lattice thermal conductivity using the acoustic phonon phase velocities in the disordered phase. In the amorphous phase, the phonons are the dominant scattering sources of heat transport and thus the Cahill model provides a reasonable approximation to the lattice conductivity of this alloy. The project was concluded and published in the *J. Optical Society of America A*. It marked the first ever publication at the honour's level by the laser spectroscopy group.
(P. Tjale, K. Singh, D. Wamwangi and B. Mathe)

Objective: Elastic properties of transition metal nitrides

Transitional metal nitride thin films have valuable properties such as chemical inertness, high thermal stability, mechanical hardness and biocompatibility, even in extreme environments, resulting in their use as protective coatings on high speed steel (HSS) for cutting applications and on bone segments and joints. Some manuscripts are at different review stages with the article on the Surface Brillouin scattering study of tantalum nitride (TaN) thin films published in the *J. Optical Society of America, A,* in 2020. The other manuscripts will be submitted to high impact factor journals in 2021. (J. Kuria, D. Wamwangi and J.D. Comins)

Objective: Properties of boron-doped amorphous carbon and diamond achieved by high fluence low energy ion implantation

This study investigates low temperature properties of boron degenerate amorphous carbon and diamond materials with p-type doping levels near the Fermi-energy E_f (i.e., localised states), via low energy and high fluence ion implantation. Initial theoretical estimations predicted a maximum T_c in the range of 140–160 K for boron-doped diamond, only taking into consideration the light atomic mass of boron, the constituent atoms and strong covalent bonds within the diamond structure. Later, complimentary predictions took into account the lattice disorder as well as the local variations of boron concentrations with local electron-phonon coupling which resulted in a $T_c \approx$ 55–80 K for 10–20% of electrically active boron. Further predictions by Cohen suggested a possible T_c maximum of 290 K for an ideal case with strong phonon-electron coupling strengths within a phonon-mediated superconducting diamond. PhD student Mahonisi received training on creating metallic contacts to diamond using electron beam lithography at facilities at UCT and training on the PPMS at Wits university. Unfortunately, there were delays in the implantation program due to COVID-19 restrictions. (N. Mahonisi, S.R. Naidoo and M. Blumenthal)