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Germanium vacancy centre formation in CVD nanocrystalline diamond using a solid dopant source

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A R T I C L E I N F O

Keywords:
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A B S T R A C T

We report the in-situ formation of germanium vacancy (GeV) centres in nanocrystalline diamond (NCD) using chemical vapor deposition (CVD) technique. Commercial Ge wafers are used as the solid dopant source and as substrate. The hydrogen-rich plasma (1% CH_4 in H_2, 3000 W and 45 Torr, ASTeX 6500 series deposition system) etches the Ge substrate and introduces the GeV complex in the NCD layer. As the melting proximity of Ge and CVD diamond growth temperature introduces limitations; the NCD depositions are restricted to (720 ± 20)°C. Scanning electron microscopy reveal randomly facetted film morphology and Raman measurements confirm diamond formation under the chosen deposition conditions.
We discuss an additional challenge, the absence of carbide layer at the Ge-NCD interface, potentially limiting film adhesion to the Ge substrate but at the same time demonstrate self-delaminating free-standing multicrystalline diamond films. Qualitative analysis using time of flight secondary mass ion spectroscopy confirms Ge incorporation, and room temperature photoluminescence (PL) measurements confirm local GeV ensemble formation in diamond films as indicated by the 602 nm PL peak. We also discuss the challenges in using NCD, present low-temperature (10*K*) PL results and assign strain to explain GeV peak shifts in such material.

Video to this article can be found online at https://doi.org/10.1016/j.sctalk.2023.100157.

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Figures and tables

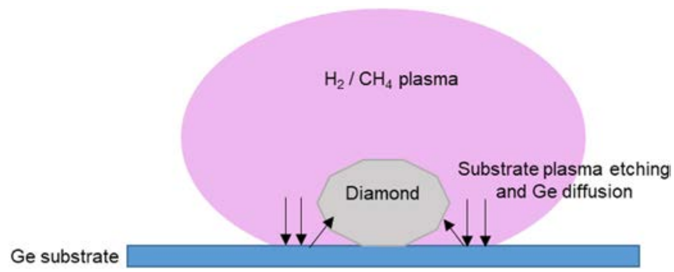

Fig. 1. Schematic for the Ge vacancy formation in CVD diamond via Ge substrate etching.Ge- germanium, GeV – germanium vacancy.

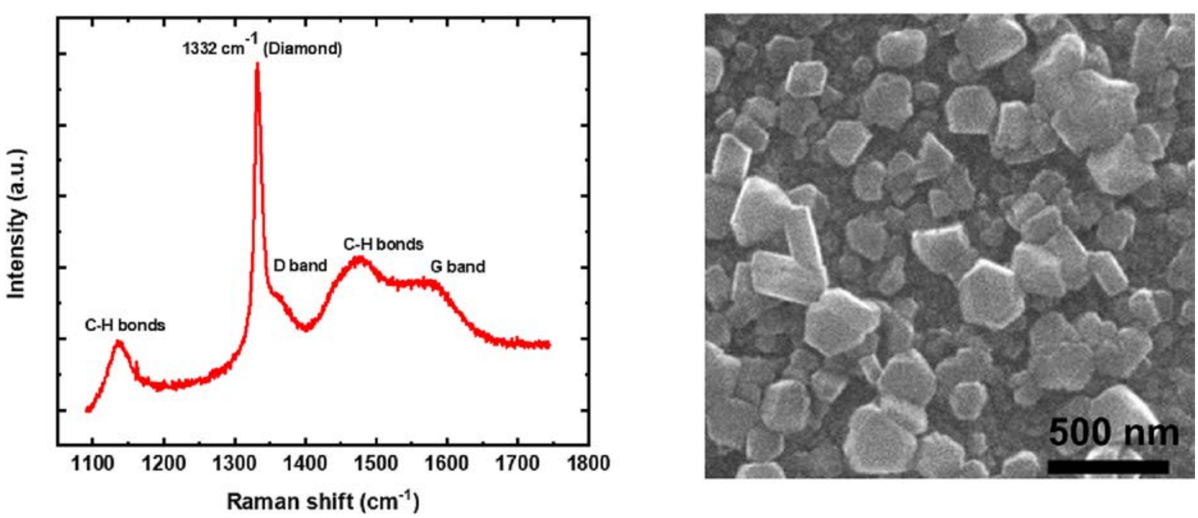

Fig. 2. Representative Raman and SEM image of a 100 nm thick NCD film. SEM – Scanning electron microscopy, NCD- nanocrystalline diamond.

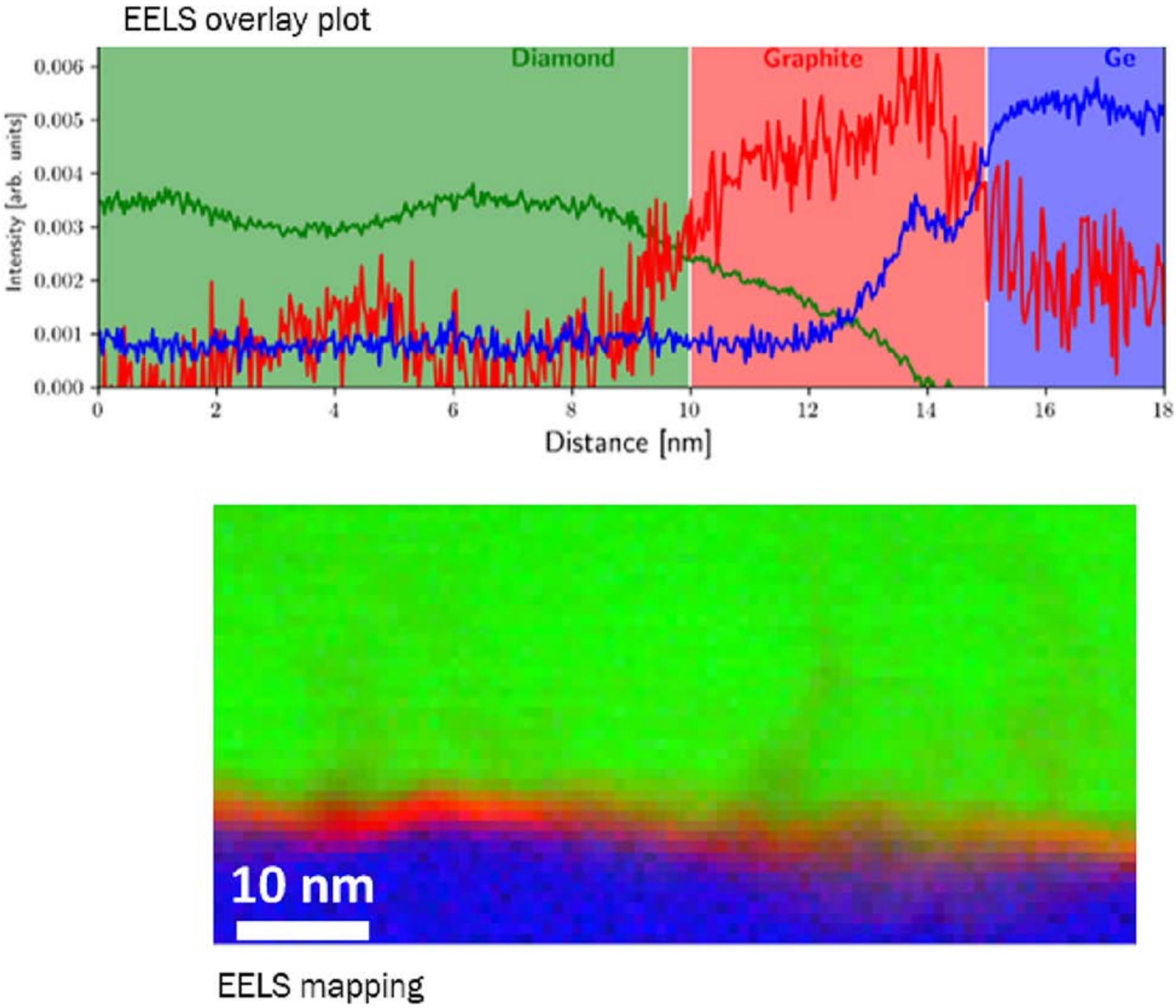

Fig. 3. EELS overlay and mapping of the NCD / Ge interface. EELS - Electron Energy Loss Spectra, NCD – nanocrystalline diamond, Ge – germanium.

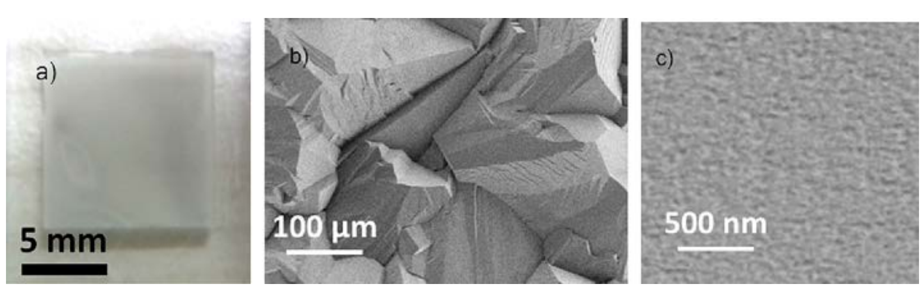

Fig. 4. (a) Optical image of the free-standing microcrystalline diamond film (1×1 cm^2) and corresponding SEM images: (b) the growth and (c) nucleation sides show different film morphologies.

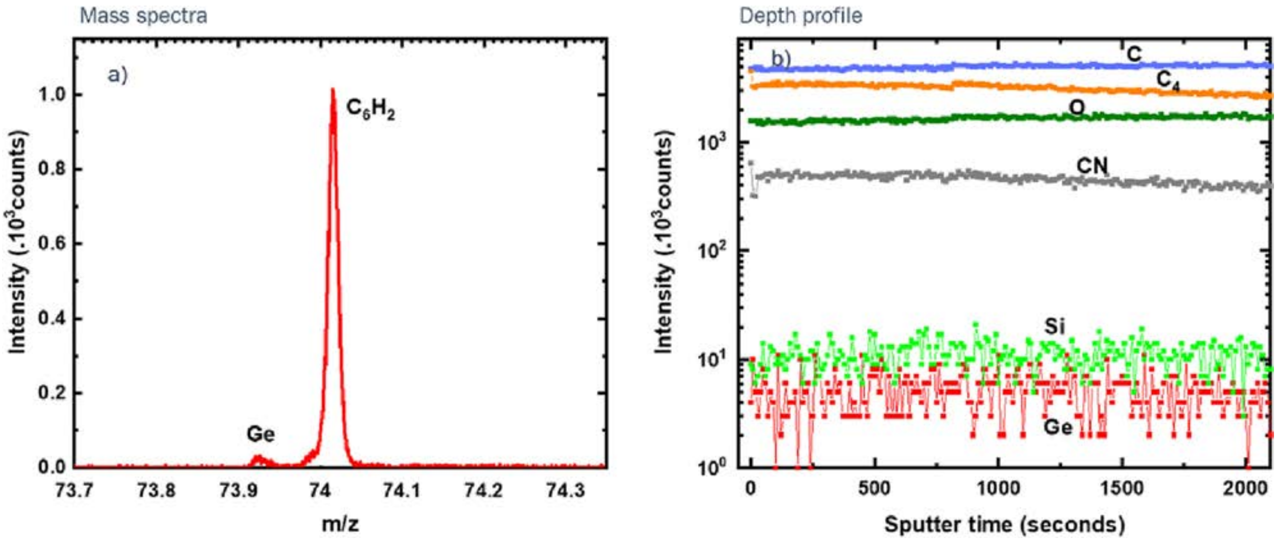

Fig. 5. ToF-SIMS measurements of the free-standing microcrystalline diamond film (a) mass/charge (*m/z*) spectrum at different positions (edges and centre) and (b) the depth profile at an edge position.

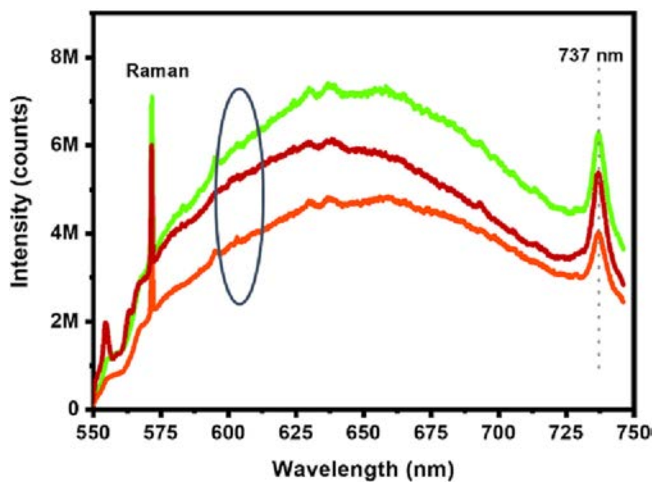

Fig. 6. Typical RT PL spectra of the free-standing microcrystalline diamond film. Measurements are carried out at multiple positions on the nucleation side of the sample.

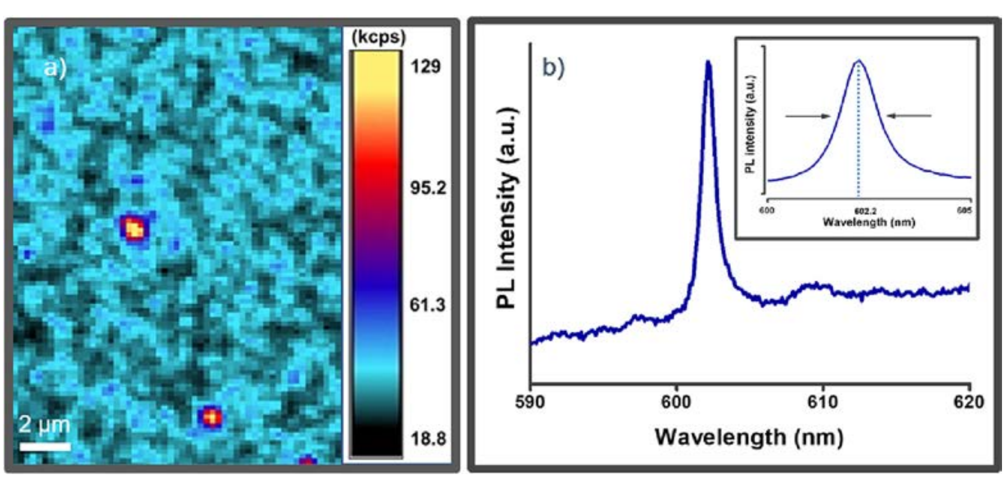

Fig. 7. RT PL mapping of 100 nm thick NCD film with band-pass filter and (b) an exemplary spectrum with intense ZPL peak measured at a bright spot in the PL mapping.

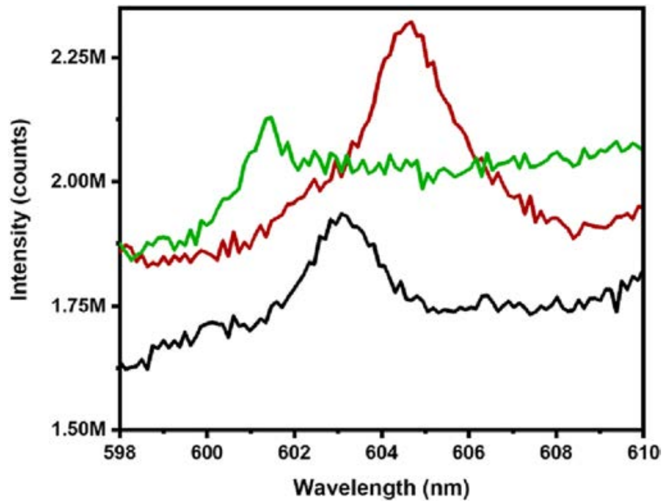

Fig. 8. Examples of typical RT PL spectra with variations in peak positions on a 100 nm thick NCD film. Measurements are carried out at random positions on the sample.

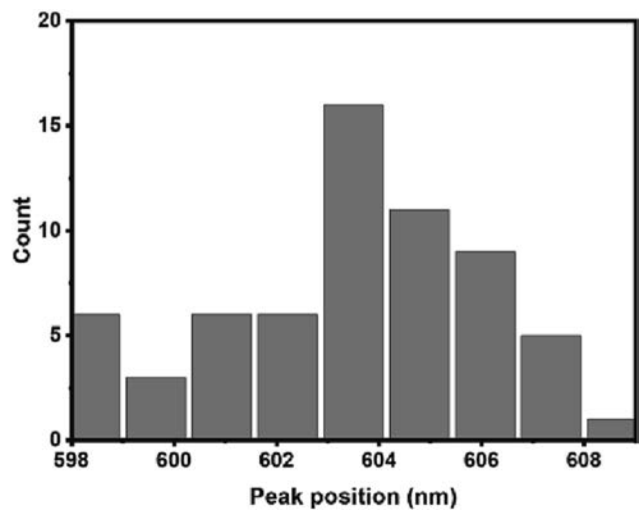

Fig. 9. The observed peak position distribution based on room temperature PL measurements on a 100 nm thick NCD film.

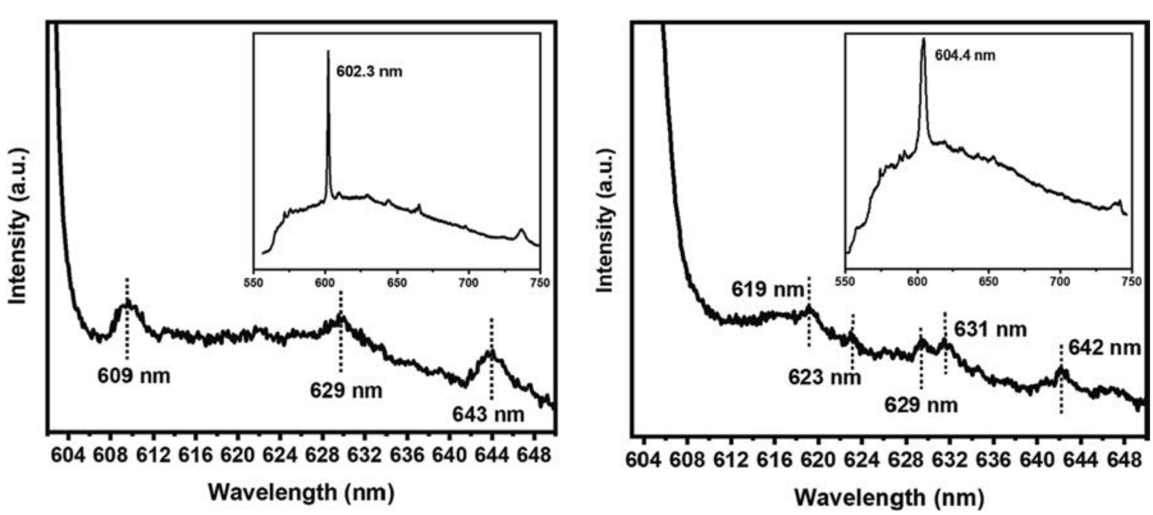

Fig. 10. Examples of RT PL spectra showing different side bands on a 100 nm thick NCD film.

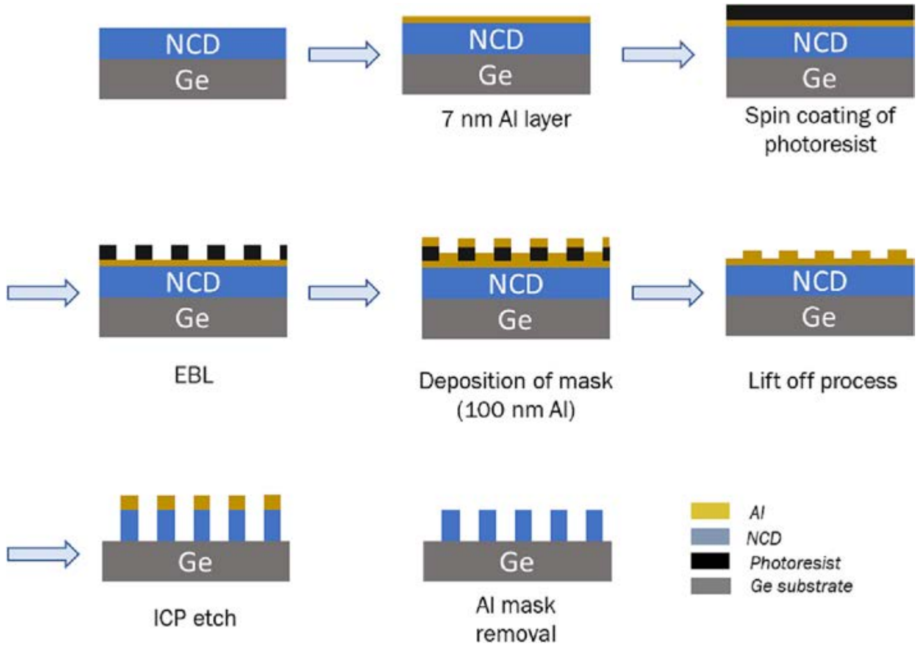

Fig. 11. Process flow for the structuring process of nanopillars in NCD.

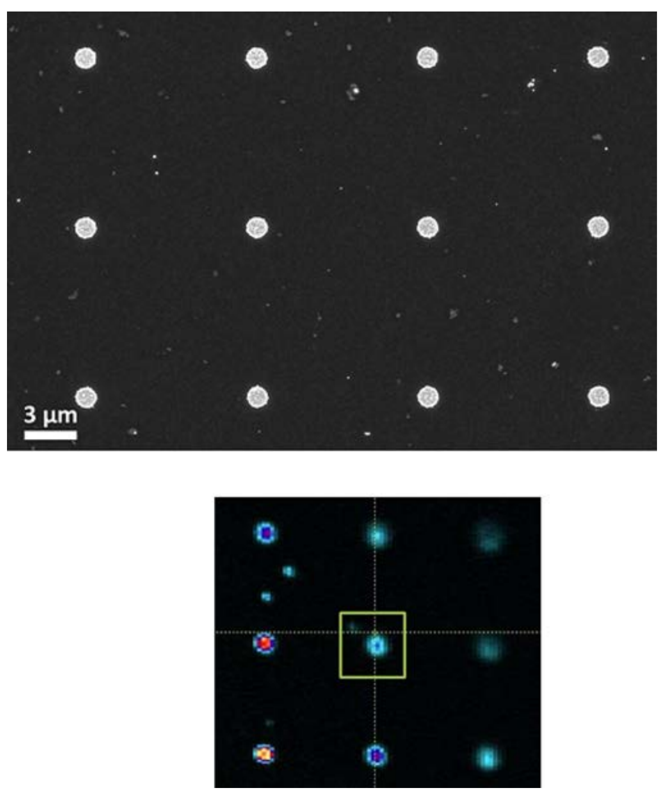

Fig. 12. Representative SEM image (top) and the room temperature PL mapping of the NCD pillars.

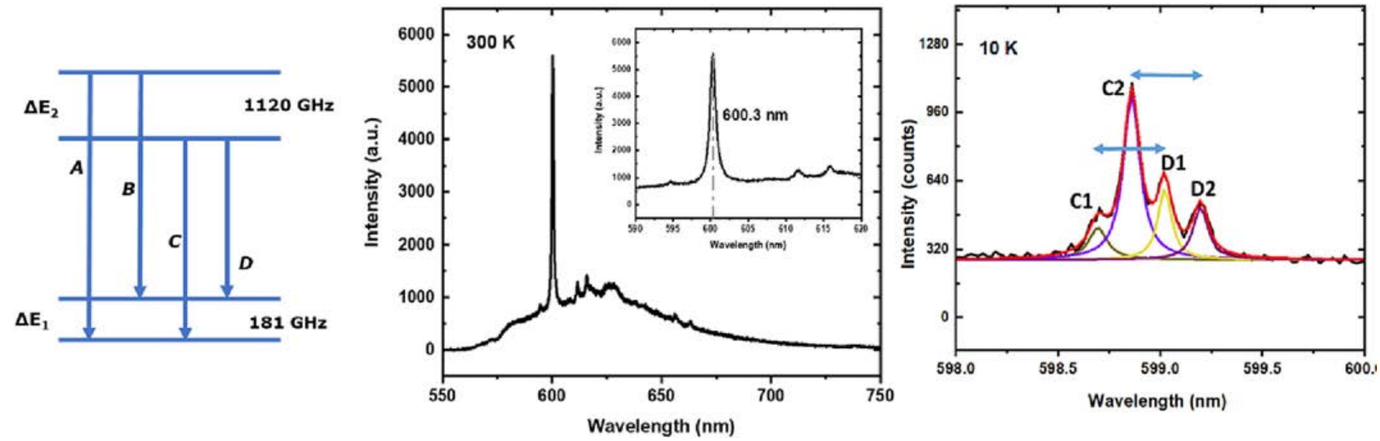

Fig. 13. Representation of the energy level scheme for the GeV centre (left), room temperature (centre) and (right) low temperature (10 K) PL spectra recorded on a GeV containing NCD pillar.

CRediT authorship contribution statement

Rani Mary Joy: Conceptualization, Methodology, Validation, Investigation, Data curation, Formal analysis, Writing – original draft, Writing – review & editing, Visualization. **Paulius Pobedinskas:** Conceptualization, Investigation, Data curation, Validation, Writing – review & editing, Supervision. **Emilie Bourgeois:** Investigation, Data curation, Validation. **Tanmoy Chakraborty:** Investigation, Data curation. **Johannes Görlitz:** Investigation, Data curation. **Dennis Herrmann:** Investigation, Data curation. **Celine Noël:** Investigation, Data curation. **Julia Heupel:** Investigation, Data curation. **Daen Jannis:** Investigation, Data curation. **Nicolas Gauquelin:** Investigation, Data curation. **Jan D'Haen:** Investigation, Data curation, Resources. **Johan Verbeeck:** Supervision, Resources. **Cyril Popov:** Supervision, Resources, Funding acquisition. **Laurent Houssiau:** Data curation, Formal analysis, Resources. **Christoph Becher:** Supervision, Resources. **Milos Nesládek:** Supervision, Resources. **Ken Haenen:** Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Data availability

Data will be made available on request.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Further reading

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Rani Mary Joy holds a Bachelor degree in electrical and electronics engineering (University of Calicut, India) and master's degree in microelectronics from TU Delft, The Netherlands. During her master's project research at Else Kooi lab she focussed on low temperature solid state epitaxy of silicon. She then joined the Dutch high tech industry as process development engineer for PECVD silicon oxide and zinc oxide deposition for solar applications. Later, at the national centre for flexible electronics in the Indian Institute of Technology Kanpur her research was on thin film transistor fabrication on flexible substrates. She joined the Wide Band Gap Materials Group of Prof. Ken Haenen in 2018 as a PhD student. Her research topic focuses on growth studies of color centres in diamond, in particular, germanium vacancy centres in CVD diamond. In addition, she also investigates stress evolution and mechanical properties of nanocrystalline diamond films.

Paulius Pobedinskas is currently a research coordinator within the Wide Band Gap Materials research group, where in 2012 he obtained his PhD degree in physics on the sputter deposition and characterization of AlN thin films. Paulius' background is in CVD diamond and III-V nitrides, synthesis and processing, structural and mechanical analysis of thin films, nanoscale physics and numerical modelling. He has experience in the deposition of polycrystalline diamond films on a wide variety of substrates. He has expertise in designing and developing photolithography process for diamond based devices. On the numerical modelling domain, Paulius has knowledge in finite element analysis. Since 2016, he is lecturing Hydrodynamics, and since 2020 Solid State Physics course at Universiteit Hasselt.

Emilie Bourgeois received her master's degree in engineering from Mines ParisTech (France) in 2006 and her Ph.D. degree in physics from the University of Paris-Saclay (Paris XI, France) in 2010. Since 2011, she has been working as a researcher at IMO-IMOMEC (Imec and Hasselt University, Belgium). Her current research interest is the optical and photoelectric characterization of materials for photovoltaic and photonics applications, and in particular the study of color center photophysics in diamond. Her recent work has focused on the establishment and optimization of a photoelectric method for the readout of NV centers spin.

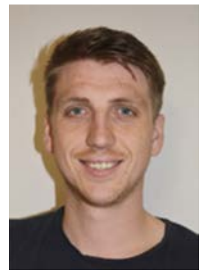
Dr. Tanmoy Chakraborty pursued his Ph.D. in IISER-Kolkata. During his Ph.D., he experimentally investigated quantum correlations and magnetic field-induced quantum level crossing in spin ½ quantum magnets. After finishing his Ph.D. in 2015, Tanmoy joined TU Dortmund (with Prof. Dieter Suter) as a postdoc where his projects dealt with engineering the states of a quantum register associated with a single nitrogen-vacancy (NV) center and performing spectroscopic characterization of NVs to test their quantum sensing efficiencies. He continued working on NV and other defect centers in the diamond during his subsequent postdocs in Stockholm University, Sweden, and Hasselt University, Belgium. Tanmoy joined QuTech - TU Delft, Netherlands in February 2020 as a postdoc (With Prof. Wolfgang Tittel and in a collaborative project with Prof. Ronald Hanson). In QuTech he has been working on the experimental implementation of a frequency multiplexed quantum repeater scheme and a hybrid quantum network scheme.

Dr. Johannes Görlitz studied physics in Saarbrücken. During his PhD (2017–2022) in the workgroup of Christoph Becher, he focused on researching the recently discovered tin-vacancy centre in diamond. This included a detailed spectroscopic study, investigation of the tin-vacancy centre's charge and spin dynamics as well as two-photon interference of single photons emitted by a tin-vacancy centre. Today, he is working at the project management agency "Projektträger Jülich", focusing on projects concerning the transformation of power grids, power storage and digitalisation with respect to the energy transition necessary to mitigate climate change.

Dennis Herrmann completed his master's thesis in the field of spectroscopy of SnV centres in diamond at Saarland University in 2019 and has since worked on optimising the optical and spin coherence of SnV centres and the experimental implementation of a spin-photon interface as a building block for quantum networks.

Celine Noël obtained her Ph.D. in Physics at the University of Namur, Belgium. Her work entitled "Depth profiling of hybrid multilayers using ToF-SIMS: from model samples to photonic devices" was directed to the understanding of failure and aging mechanisms in organic electronic and photovoltaic devices. After her Ph.D., Céline joined Imec (Leuven, Belgium) in 2020 as a researcher within the Material and Component Analysis Department. Aside from conducting research projects in microelectronics, she performs surface analyses using a wide range of characterization techniques (e.g. ToF-SIMS, SSRM, AFM, C-AFM), supporting the imec cleanroom with failure analysis and metrology.

Julia Heupel graduated in October 2018 as Master of Science in the Nanoscience degree program of the University of Kassel. Since November 2018 she is working as a staff scientist on the topic "Diamond Photonics" in the Institute of Nanostructure Technologies Analytics in the "NanoDiamond" group of apl. Prof. Dr. Cyril Popov of the University of Kassel.



Daen Jannis received his Bachelor's and Master's degree in Physics at the KU Leuven. In 2021, he received his PhD degree from the University of Antwerp at the Electron Microscopy for Materials Science (EMAT) group under the supervision of Prof. Dr. Jo Verbeeck. Currently, he is working as a post-doctoral researcher at EMAT.

Nicolas Gauquelin completed his studies in Materials Science and Solid-State Chemistry at the university of Rennes 1 (France). After completing his studies in 2005, he started a PhD in Physical Chemistry at the laboratory for Solid State Ionics in the RWTH Aachen in Aachen, Germany and graduated with honours in 2010. He then moved to the Canadian Centre for Electron Microscopy in McMaster University in Hamilton, Canada. There, he developed skills in pushing electron microscopy to its frontiers using aberration corrected microscopes studying complex layered oxides and thin film heterostructures by atomically resolved EELS and HAADF STEM imaging. In 2013, he joined EMAT in Antwerp (Belgium) to polish his skills and refine his knowledge on Fine structure analysis of interfaces and developing new spectroscopies as well as applying imaging and spectroscopy techniques in-situ and in-operando to physical processes such as ferroelectric switching, metal-insulator transition. His work yielded to almost 100 publications from which >30 in high impact factor journals (IF>8).

Jan D'Haen, born in 1965, started as electron microscopist in 1987 at the former LUC. After obtaining his PhD in 1996, he became in imo-imomec responsible for mainly electron microscopy based analytical services for internal and external research projects. Since 2015 he is appointed as Full Professor. He is the head of the Analytical & Microscopical Services (AMS) expertise group, which focuses mainly on microscopical and/or diffraction based analyses to support researchers within imo-imomec in the development of new material systems and third party researchers and companies.

Johan Verbeeck received his PhD degree (2002) from the University of Antwerp. Currently he is a full Professor at the electron microscopy group (EMAT) of the University of Antwerp. Johan Verbeeck is an expert in the field of transmission electron microscopy and electron energy loss spectroscopy focusing both on applications in state of the art materials science as well as on developing new techniques. He is the author of >200 ISI contributions with over 3600 citations. In 2011, he received the prestigious Ernst Ruska award for electron microscopy for his contribution to the quantification of EELS spectra and the development of electron vortex beams. He is the author of the EELSMODEL software providing model based quantification to users worldwide. In 2012 he received an ERC starting grant in order to explore the properties of electron vortex waves and he is currently expanding this research towards versatile programmable phase plates in the TEM.

Cyril Popov has received his MSc in Chemical Engineering in 1990 and PhD in 1994 from the University of Chemical Technology and Metallurgy, Sofia, Bulgaria. In the period 1995–1997 he was a postdoc at the National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan financially supported the Japan Society for the Promotion of Science (JSPS) and at the Central Laboratory of Photoprocesses, Bulgarian Academy of Sciences, Sofia, working on preparation and investigation of novel materials in the ternary system B-C-N. In 1998 he joined the Institute of Nanostructure Technologies and Analytics (INA), University of Kassel, where at the present he is professor and leader of the Nano Diamond Group. His current research interests cover the deposition, characterization and applications of nano- and ultrananocrystalline diamond films. He is an author of over 150 publications and editor of 6 books.

Laurent Houssiau holds a Civil Engineering degree and a PhD in Engineering from the Catholic University of Louvain (UCLouvain). He has been a professor at the University of Namur (UNamur) since 2000 and is currently head of the Physics Department. His research expertise includes the analysis of surfaces and interfaces, as well as plasma treatment and deposition of materials in vacuum.

Christoph Becher is a full professor of physics at Saarland University, Saarbrücken, Germany, leading the quantum optics research group. He received his PhD in physics from University of Kaiserslautern, Germany, in 1998 working on generation of non-classical light from semiconductor lasers. Christoph Becher held two postdoctoral positions: at University of California, Santa Barbara (1999–2000) with the first demonstration of single photon emission from self-assembled semiconductor quantum dots and cavity-QED experiments; at University of Innsbruck, Austria (2001–2005), he was part of the team demonstrating the first quantum gate with trapped ions, generation of multi-ion entangled states, implementation of simple quantum algorithms and cavity QED with trapped ions. His research interests are in the field of quantum technologies for quantum communication & sensing, in particular exploration of color centers in diamond as quantum bits, single photon sources and for quantum sensing applications; diamond-based micro-resonators and single photon nonlinear optics, e.g. quantum frequency conversion for quantum networks.

Prof. Milos Nesládek, Ph.D., obtained his MSc. degree from the Faculty of Mathematics and Physics at Charles University in Prague, and his Ph.D. degree from the Czech Academic Sciences, in collaboration with KU Leuven in the field of electronic transport and quantum condensed matter. He is a professor of physics at the University of Hasselt and a guest professor at IMEC, Belgium. He is one of the pioneering scientists in the growth of CVD diamond crystals in all forms. Prof. Nesladek's research topic deals with photoconduction in condensed matter systems with an emphasis on wide-bandgap semiconductors. He is active in Quantum Science and Technology field, an example of his research is developing photoelectrically-read solid-state Qubits in diamond based on paramagnetic spin centers for applications to quantum sensing and metrology.

Prof. Nesladek has participated in several EU projects ranging from basic physics to industrial development projects, or Quantum Flagship projects, some of which he has coordinated. Prof. Nesladek is a member of several conference boards, and he is the Belgian representative to the Quantum Community Network (QCN) of the Quantum Flagship. Prof. Nesladek published over 300 scientific papers and contributed to several books. He is an associated editor of Diamond Related Materials and a member of the editorial board of Advanced Quantum Materials and Applied Sciences.

Ken Haenen is a material physicist and the current vice rector of Hasselt University. He obtained his doctorate in 2002, and after six years as a FWO postdoctoral researcher, including a period in Tsukuba, Japan, at the NIMS, he was appointed tenure track lecturer in 2008 and then full professor since 2019. He leads the research group of Wide Band Gap Materials (WBGM) within imo-imomec, where his research interests focus on CVD diamond, including deposition, opto-electronic characterization, surface functionalisation, and diamond-based devices as part of a broader scope examining carbon materials for power generation and conversion. He is also Editor-in-Chief of the magazines "Diamond and Related Materials" and "MethodsX" (Materials Science), and is a member of the editorial board of "Scientific Reports and Physica Status Solidi". He is involved in the organisation of several leading international diamond and nanocarbon conferences, the International Conference on Diamond and Carbon Materials (Chair), Hasselt Diamond Workshop (Co-Chair), and New Diamond and Nano Carbons (Executive Committee).