



Bottom up engineering of single crystal diamond membranes with germanium vacancy color centers

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Abstract: Color centers in diamond have garnered significant attention for applications in integrated quantum photonics. The availability of thin (~ hundred of nanometers) diamond membranes is paramount to achieve this goal. In this paper, we describe in detail a robust, reproducible and cost effective fabrication method that enables engineering high quality thin diamond membranes with uniform distribution of germanium vacancies employing microwave plasma chemical vapor deposition. We use a combination of different germanium precursors for homogeneous doping of the membranes to increase the probability of germanium incorporation into the diamond lattice. Our fabrication methodology can be further extended to implementation of other color centers in thin diamond membranes and be used for engineering quantum photonic devices.

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1. Main text

The recent improvements in the growth techniques and availability of synthetic diamonds enabled the development of new engineering materials for advanced, electronic, thermal, and quantum applications [1–4]. The latter is particularly motivated by the availability of color centers in diamond that act as single photon sources [5]. In particular, the recent focus on group IV - vacancy defects (e.g. silicon, germanium, tin or lead vacancies) has spurred a new wave of research into generation of these color centers [6]. One of the key goals is to integrate these color centers with photonic resonators such as microdisks and photonic crystal cavities [7–9]. The fabrication of the resonators require large scale, thin diamond membranes that are used as the building block for the resonators.

Whilst the fabrication processes of diamond membranes have been significantly refined over the last several years resulting in robust and mature technology [10–17], the homogeneous in-situ doping of diamond membranes with new color centers presents still a major challenge. While doping of some of the elements (e.g. Ge or Si) [18,19] is possible during high pressure high temperature growth (HPHT), this method is not applicable to membranes, as they would shutter under the severe conditions. Other avenue that has been explored is ion implantation [20–24]. However, this often results in non ideal emission lines (broadened and enhanced spectral diffusion), due to residual strain that cannot be fully recovered using standard high temperature annealing. HPHT annealing has been shown to brighten some of the group IV defects and make the luminescence lines narrower (e.g. SnV)²¹, but it cannot be used for diamond membranes due to their small thickness.

Alternatively, bottom up doping during growth is a promising avenue to incorporate fluorescent color centers [25]. This method has been explored widely to incorporate the SiV- color centers into growing diamond, primarily due to similar atomic properties and relatively comparable atomic size. Due to the presence of silicon in most chemical vapor deposition (CVD) chambers,

either due to use of silicon as a substrate or due to the quartz walls, silicon is often incorporated into the growing diamond.

In this work we investigate the possibility of homogeneous incorporation of germanium vacancies (GeV) color centers into diamond membranes using microwave plasma CVD (MPCVD) process. GeV color centers possess similar defect configuration to the SiV, but has a larger energy splitting in ground state compared to SiV- (~ 170 GHz). The zero phonon line (ZPL) of the GeV is around 602 nm, and it is envisioned to possess a higher fluorescence quantum yield. All above mentioned characteristics make this color center appealing for quantum information processing applications⁶.

The overgrowth of diamond using MPCVD process involves volatile chemicals and many surface reactions of a vapor phase and dissociation of H_2 and CH_4 to produce gaseous precursors necessary for the diamond growth. As schematically illustrated in Fig. 1(a), diamond layer forms from an activated mixture of hydrocarbon gases and hydrogen. Incorporation of impurities during growth can also happen at the same time. To incorporate germanium into diamond membrane, we studied three different approaches using pure metallic germanium, germanium oxide (GeO_2) or the combination of the metallic and oxide precursors. The germanium sources were positioned in close proximity to the membranes during the growth, as explained below.

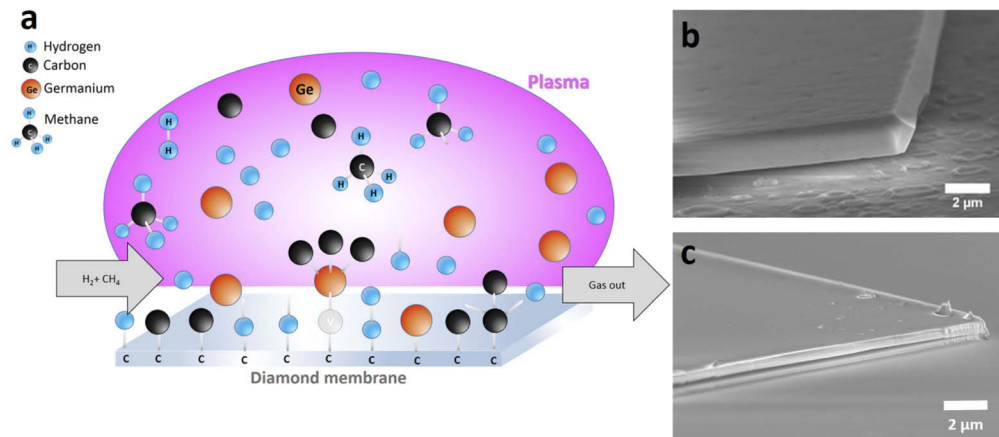


Fig. 1. a) Incorporation of Germanium during MPCVD growth of diamond. The precursors are dissociated in the plasma region, creating active species which will eventually incorporate into the growing diamond. b) Representative SEM image of a thick 1.7 μm and c) a thin diamond membrane ~ 300 nm.

The diamond membranes were generated using ion implantation and liftoff, as described in detail elsewhere. Briefly, a type IIa (100) single-crystal diamond (Element six) was implanted with helium ions at 1 MeV with 5×10^{16} ions/cm² followed by 900°C high vacuum annealing for 1 hour. The sample was then immersed in deionized water and a constant voltage of 60 V to lift-off of the membranes was applied. An SEM images of a 1.7 μm thick diamond membrane is shown in Fig. 1(b). After each growth, the membrane was flipped and thinned to ~ 300 - 500 nm using Inductively Coupled - Plasma Reactive Ion Etching (ICP-RIE) to remove the original damaged membrane. The etching takes place in the presence of Argon, Oxygen and SF_6 at 45 mTorr with ICP power of 500 W and RIE of 100 W for 18 minutes to reach the required thickness. An SEM image of a thinned diamond membrane of ~ 300 nm is shown in Fig. 1(c).

In the first approach to generate GeVs, 3 pieces of metallic germanium with the size of ~ 1 mm³ each, were placed on a carbon puck about 1 cm away from the diamond membrane sitting on a sapphire substrate as illustrated schematically in Fig. 2(a). The diamond membrane is located approximately in the middle of the sapphire sample that is used as a carrier. Sapphire

is chosen intentionally as it does not result in silicon contamination. The sample was then overgrown for 8 minutes at 60 Torr with 900 W of microwave power in hydrogen/methane (with the ratio of 400/4 sccm) atmosphere. An optical image of the overgrown membrane is shown in Fig. 2(b). The surface of the membrane is rough after the growth, with many secondary nucleation spots. Metallic germanium has a relatively low melting point of $\sim 937^\circ\text{C}$, that caused excessive sputtering of germanium during the growth. While on the one hand it should have been advantageous for incorporation of germanium into the growing diamond, it resulted in micromasking and induced secondary nucleation. As a result, a square pattern appeared on the diamond, as shown optically in Fig. 2(b) and in a scanning electron microscope (SEM) in Fig. 2(c).

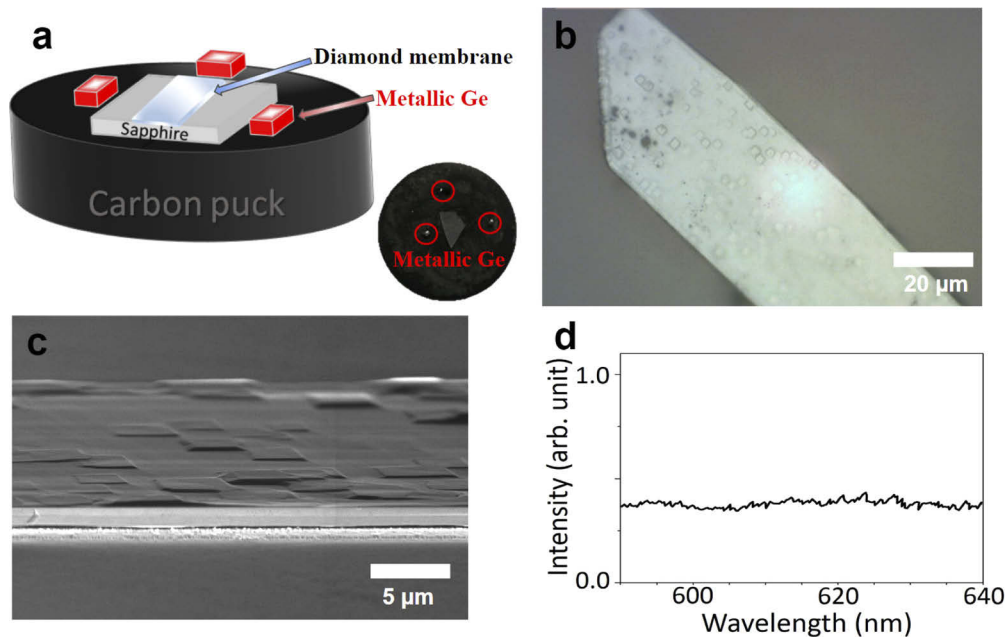


Fig. 2. Incorporation of GeV using metallic source. a) Schematic of the growth geometry of the diamond membrane and metallic sources. Inset, is the actual photograph of the puck with diameter of ~ 1 inch. b) Optical and c) SEM images of the membrane after overgrowth process in MPCVD. Visible square areas in SEM image is the result of secondary nucleation from micromasking with sputtered germanium during the growth. d) PL spectrum from the membrane after overgrowth did not show any peak at ~ 602 nm from GeV centers.

We examined the GeV incorporation using a confocal photoluminescence (PL) setup. A 532 nm laser excitation with high numerical objective ($\text{NA} = 0.9$) was used as excitation source. In this batch of diamond membranes that were overgrown with only a metallic germanium source, we could not observe any emission from GeV centers, as shown in Fig. 2(d). This could be due to vaporizing of the germanium during high temperature growth before it is embedded into the diamond structure.

To resolve the issue with the sputtering of metallic germanium, in the second approach we used germanium oxide which has higher melting temperature ($\sim 1,115^\circ\text{C}$). Three pressed germanium dioxide (GeO_2) powder pieces of 1 mm^3 size were placed about 1 cm away from the diamond membrane on a carbon puck, that undergone the same overgrowth process. This is schematically shown in Fig. 3(a). An optical image shown in Fig. 3(b) indicates the smooth growth of diamond membrane which is also evident in the SEM images of the membrane in Fig. 3(c). The smooth appearance of the membrane without secondary nucleation, confirms that the sputtering process

which happened in the first approach, has been eliminated. In addition, the PL characterization of the membrane showed the emission from GeV centers at ~ 602 nm confirming the incorporation of germanium into the membrane during the growth. However, the amount of incorporation is relatively low (as indicated by the low intensity of GeV emission) most probably due to the slow release of the Ge atoms from the oxide during the growth. Such a method could be explored in the future to incorporate single GeV defects.

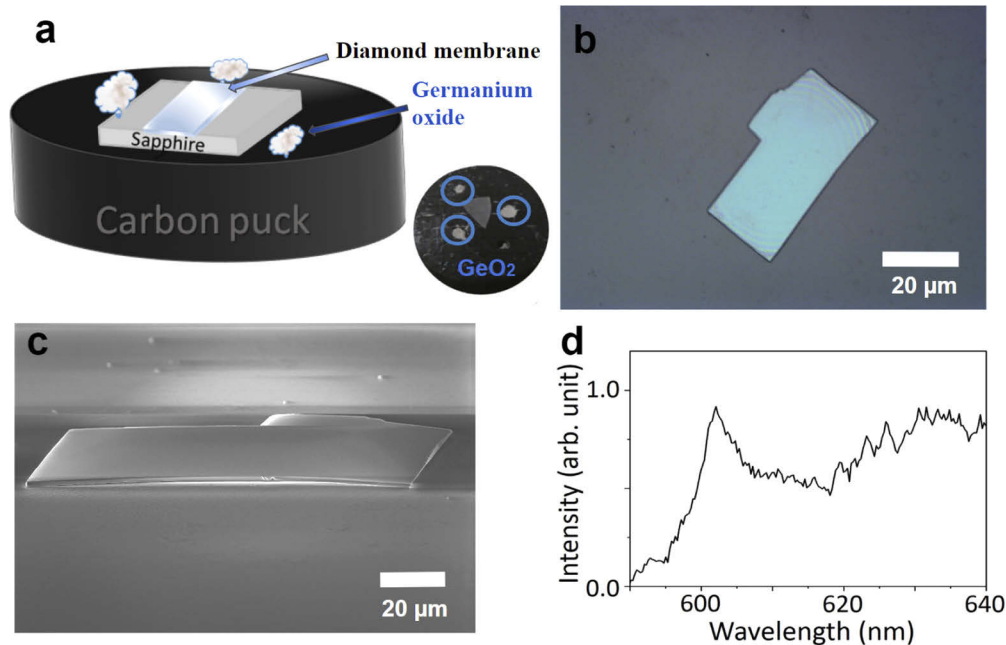


Fig. 3. Incorporation of GeV using a germanium oxide source. a) Schematic of the growth geometry of the diamond membrane and oxide sources. Inset, is the actual photograph of the puck with diameter of ~ 1 inch. b) Optical and c) SEM images of the membrane after the overgrowth, resulting in smooth surface after the growth. d) Room temperature PL spectrum of the membrane, with the peak centered at ~ 602 nm confirms the successful incorporation of GeV into the diamond membrane.

In the third approach both sources were used to incorporate more germanium into the diamond lattice. To increase the amount of germanium during the growth, 3 metallic germanium pieces of ~ 1 mm³ were placed on a carbon puck along with 3 pressed GeO₂ powder pieces with similar sizes all around the sapphire substrate which is schematically shown in Fig. 4(a). The distance of germanium sources from the membrane was chosen to be around 1.5 cm to avoid the resputtering of metallic germanium on top of the diamond surface. An optical and SEM images of the diamond membrane after the same overgrowth process are shown in Figs. 4(b) and 4(c) respectively. The membranes are mostly smooth without square patterns of nucleation. The PL spectrum recorded at room temperature from the overgrown membranes shows a bright characteristic GeV peak shown in Fig. 4(d).

The plasma chemistry changes when adding metallic germanium to the oxide resulting in higher concentration of Ge ions in the plasma and successful incorporation of germanium into diamond lattice. The presence of the oxide could passivate the metallic germanium sputtering during growth, causing a longer and more consistent release of germanium ions into the plasma. A detailed mechanism should be further explored in future studies.

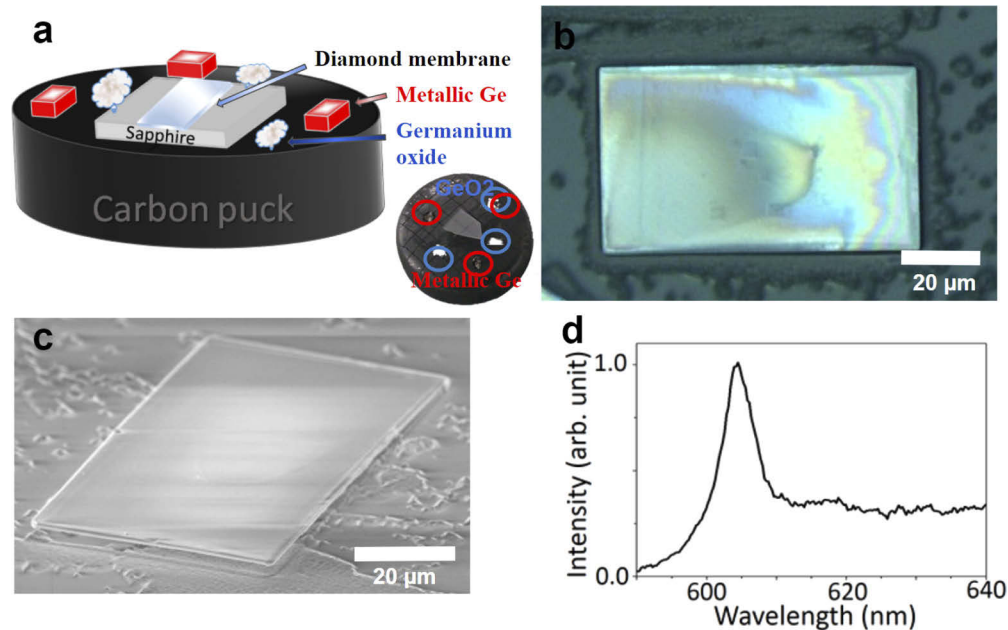


Fig. 4. Incorporation of GeV using both metallic and oxide sources. a) Schematic of the growth geometry of the diamond membrane and metallic and oxide sources with larger distance compared to the previous approaches. Inset, is the actual photograph of the puck with diameter of 1 inch. The locations of both metallic and oxide germanium sources are marked. b) Optical and c) SEM images of the membrane after overgrowth process in MPCVD indicating the smooth surface after the growth. d) The pronounce peak confirms the successful incorporation of GeV into the diamond membrane.

Table 1 summarizes the results of the three different approaches undertaken to create GeV color centers in the diamond membranes.

Table 1. Summary of the conditions used to achieve GeV color centres in thin diamond membranes

Germanium source	Growth conditions	Result
Metallic Ge	60 Torr, 900 W, 400/4 sccm H ₂ /CH ₄ for 8 min	Micromasking and no incorporation of GeV
GeO ₂ pressed powder	Same as above	Smooth surface and minimal GeV peaks
Metallic Ge, GeO ₂ pressed powder around the sample	Same as above	Smooth surface with uniform distribution of GeV across the membrane

Given the promising result of the GeV doping using a combination of the oxide and metallic sources, these membranes can be used to fabricate photonic resonators. For the proof of principle, we first recorded PL spectra at random locations across the membrane, to show that the incorporation is homogeneous within the membrane. Figure 5(a) shows three spectra that demonstrate presence of GeV color centers. An intensity confocal map from the membrane grown with the third method is shown in Fig. 5(b). The PL counts across the membrane is similar indicating the homogeneous distribution of GeV in the membrane. Next, the same membrane was patterned to fabricate microring resonators. Figure 5(c) shows the patterned ring array with a 2.5 μm outer radius and 400 nm width rings. Although the membrane still rests on a substrate,

whispering gallery modes were found in most of the rings. A representative of the PL spectrum obtained from the one of the ring cavities indicated with the red circle in Fig. 5(c), is shown in Fig. 5(d). The smaller periodic peak are corresponded to fundamental modes with average quality factor of $Q \sim 500$. The narrow bright peak at 602 nm in Fig. 5(d) is GeV zero phonon line coupled to whispering gallery modes (WGMs). The linewidth of the narrowed GeV peak is reduced in the photonic resonator to ~ 2.8 nm and the average linewidth of supported modes is ~ 1.2 nm.

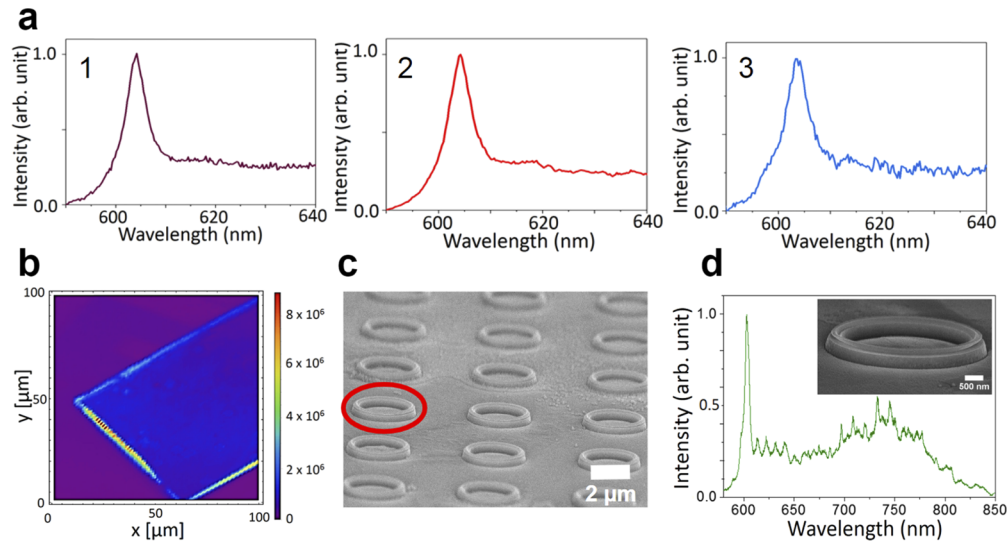


Fig. 5. a) Room temperature PL spectra collected from three random position on the diamond membrane confirming the homogeneous incorporation of GeV into diamond. b) An intensity confocal map from the membrane grown with third showing a uniform distribution of GeV in all measured points across the membrane. c) low magnification SEM image of the fabricated microring from diamond membrane containing GeV centers d) PL spectrum from the diamond showing whispering gallery modes as well as GeV peak. Inset, zoomed image of the diamond ring.

2. Conclusions

We presented details on best avenues to incorporate germanium into diamond using solid sources to generate GeV color centers, while maintaining high quality growth and smooth diamond membranes. The most promising condition for doping is the combination of metallic and oxide germanium sources. Our work can be extended by optimising the growth conditions to incorporate single GeV centers (e.g. by reducing the amount of oxide in the chamber), or employing the same technique to incorporate other group IV defects, such as tin or lead vacancies. Overall, the bottom up doping of diamond is a promising avenue as it avoids ion implantation and enables direct incorporation of color centers into a diamond membrane without damage, that can be immediately processed for photonic resonators.

Funding

Australian Research Council (DP180100077, DP190101058).

Acknowledgments

We thank Kumar Ganesan with assistance for ion implantation and Dr Mika Westerhausen for useful discussion on plasma chemistry.

Disclosures

The authors declare no conflicts of interest

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