Transferrable single crystalline 4H-SiC nanomembranes†

Munho Kim,a Jung-Hun Seo,a Deyin Zhao,b Shih-Chia Liu,b Kwangeun Kim,a Kangmook Lim,c Weidong Zhou,b Edo Waks,c and Zhenqiang Ma*a

In this work, we demonstrate a transferrable single crystalline 4H-SiC nanomembrane (SiC NM) released from a SiC-on-insulator (SiCOI) wafer. High resolution X-ray diffraction (XRD) and atomic force microscopy (AFM) were performed on the SiC NM and confirmed similarly good crystallinity and surface morphology. In addition, the refractive index and extinction coefficient of the SiC NM were investigated using ellipsometry analyses. Despite its thinness (i.e., 200 nm), the SiC NM achieved an absorption greater than 40% in the wavelength range of 200–260 nm with a maximum absorption of 73.8% at 256 nm. Our transferrable SiC NM provides not only good mechanical flexibility, but also exhibits excellent ultraviolet (UV) light absorption which could be readily utilized for high sensitivity flexible UV detectors.

1. Introduction

Ultraviolet (UV) sensors are an indispensable element in a wide spectrum of commercial and military applications such as water and air purification, UV missile guidance systems, and security systems.1–3 Typically, UV sensors are required to operate under harsh conditions and in complicated gaseous environments. Therefore, wide band gap semiconductors, including SiC, GaN, and metal-oxide materials (e.g., ZnO, β-Ga2O3, and SnO2) from thin film to one-dimensional (1D) nanostructures, are favorable materials due to their large band gap energy.4,5 However, photodetectors based on metal-oxide materials suffer from a slow response and poor photocurrent stability because of their natural defects.6–8 Also, 1D nanostructured UV photodetectors show unstable performance at high temperatures due to strong surface states that originated from a large surface area-to-volume ratio.5 Moreover, the thermal conductivity of GaN (i.e., 1.3 W cm−1 K−1) is almost one-fourth of SiC (i.e., 4.9 W cm−1 K−1) and even lower than that of Si (i.e., 1.5 W cm−1 K−1).9 Poor thermal conductivity limits the operation of GaN photodetectors at high temperature and causes device aging.10 On the other hand, single crystalline SiC with 4H hexagonal polytype (4H-SiC) has excellent material properties for UV photodetectors, such as a bandgap energy of 3.23 eV at 300 K and a high thermal conductivity of 4.9 W cm−1 K−1 which can overcome the issues mentioned above.9 However, the fabrication of SiC photodetectors has been only available on rigid substrates, so that they always have a planar format. Flexible UV photodetectors using thin SiC films can not only retain their bendability and light weight, but also exhibit desirable performance in hostile environments attributed to the material advantages mentioned above. 1D nanostructures of SiC such as nanowires and nanoneedles may offer a platform for flexible applications, but their device performance at high temperature will be limited.9 On the other hand, transferrable 4H-SiC nanomembranes (4H-SiC NMs) can create a wider range of high performance UV detectors which exhibit favorable mechanical flexibility and thermal properties. Nanomembranes of GaN, ZnO, and β-Ga2O3 have been reported,11–14 but the 4H-SiC NM has not yet been reported. Although various material platforms (i.e., ZnO, β-Ga2O3, and SnO2) have been studied as candidates for flexible UV photodetectors, none of them achieved long term and high temperature stability. Thus, SiC NMs can offer excellent stability as well as high performance in future UV detection systems.

In this study, we have demonstrated a transferrable single crystalline SiC NM from the SiC-on-insulator (SiCOI) wafer. The SiC NM was released from the SiCOI wafer by selective etching of the buried oxide layer and subsequently transferred onto the flexible substrate. The optical properties of the SiC NM were carefully examined. The results show that over 40% of incident light was absorbed by the SiC NM in the wavelength range of 200–260 nm. Our work demonstrates that the transferrable SiC NM efficiently absorbs UV light, thus establishing the SiC NM as a promising candidate for flexible UV photodetectors.

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6tc04480h
2. Results and discussion

A thin film delamination technology has been applied for various semiconductors such as Si and Ge to integrate a single crystalline thin layer on top of the insulator.15,16 Smart-Cut® based on hydrogen (H) ion implantation and wafer bonding is the most practical and cost effective method to fabricate the SiCOI wafer.17 An exfoliation of the single crystalline 4H-SiC thin film from the bulk SiC wafer is completed by H⁺ ion implantation and subsequent annealing. The fabrication process of the SiCOI wafer as shown in Fig. 1 can be found in the experimental section. Fig. 2(a) shows an optical image of the fabricated SiCOI wafer. As shown in Fig. S1 (ESI†), the continuous SiC layer was split from the SiC wafer after annealing at 1050 °C, while small SiC flakes were only formed after annealing at 850 °C and 950 °C. Most of the SiC area from the bonded SiC layer was successfully transferred onto the oxidized Si substrate without voids or defects. Fig. 2(b) shows a top view microscopy image taken from the SiC layer with etching hole patterns of the SiCOI wafer. The inset shows the microscopy image of the SiC NM after the completion of the releasing process. Irregular bright spots are due to trapped air or HF solution under the SiC NM. These spots were diminished after the SiC NM transfer. Fig. 2(c) and (d) show the optical and microscopy zoomed-in images of the transferred SiC NM on the PET substrate. No wrinkles or fractures on the transferred NM were observed.

The as-split SiC layer was etched by the ICP–RIE with a gas mixture of BCl₃/Cl₂/Ar at 2 mTorr chamber pressure. ICP and RIE power were kept constant at 250 W and 300 W, respectively. Fig. 3(a) shows the surface roughness of the SiC layer before (i.e., as-split) and after etching (i.e., as-etched) and etching rates associated with the gas flow of BCl₃. The thickness of the etched SiC was carefully measured by Tencor AlphaStep 200. The root-mean-square (RMS) surface roughness (Rq) of the as-split SiC layer was measured to be 3.99 nm, while it was reduced to 2.95 and 2.39 nm measured from the etched surface of the SiC using a BCl₃ flow of 10 and 20 sccm, respectively. Fig. 3(b)–(d) show three dimensional (3D) AFM images of the as-split and as-etched SiC surfaces. As shown in the AFM images, smoother surfaces were obtained by increasing the BCl₃ flow rate. Such an improvement in surface roughness may be ascribed to the use of BCl₃ which eliminates water vapor and residual oxygen from the etching chamber.18 It was reported that a BCl₃ concentration of 55% in the gas mixture promoted smoothing of the etched surface by increasing density of heavier ions BCl⁵⁺ and BCl⁷⁺ which results in angular sputtering and faster removal of sharp features.19 The etching rate was slightly increased from 48.3 to 51.5 nm min⁻¹ when BCl₃ was increased from 10 to 20 sccm. Thus, the ICP–RIE provides a much faster etching rate compared to that (i.e., MRR) of the CMP with moderate resultant surface roughness. It should be noted that a similar value of Rq (i.e., 2.39 nm) in the case of the as-etched SiC was measured from the transferred SiC NM. A detailed
analysis of the surface conditions and chemical composition of the SiC can be found in Fig. S2 (ESI†).

The crystal quality of the SiC layer of the finished SiCOI wafer was characterized by XRD. Fig. 4 shows the (0 0 0 4) reflection X-ray rocking curves of the as-etched SiC layer and the bulk SiC wafer. A full width at half-maximum (FWHM) of 30 arcsec was obtained for the bulk SiC wafer. However, the FWHM of the rocking curve of the SiC layer of the SiCOI wafer was measured to be 120 arcsec. The wider FWHM value may indicate that the crystal quality of the SiC layer was degraded due to vacancies and residual H+ ions which remained inside the SiC layer after layer splitting. In addition, it is reported that defects could be created by the large implanted dose of H+ ions (i.e., \(1 \times 10^{16} \text{ to } 1 \times 10^{17} \text{ cm}^{-2}\)) required for the fabrication of the SiCOI wafer.20 It should be noted that a similar FWHM value (i.e., 120 arcsec) was measured for the SiC NM transferred onto the PET substrate.

To perform optical characterization of the SiC layer of the SiCOI wafer, optical constants (i.e., refractive index and extinction coefficient) were measured by using the ellipsometer in the wavelength range of 200–1600 nm. Fig. 5(a) and (b) show the refractive index and extinction coefficient taken from the SiCOI wafer. The inset shows the magnified spectrum at a wavelength of 200–500 nm. Since the SiO2 layer exists under the top SiC layer of the SiCOI, the refractive index and extinction coefficient of the SiO2 were taken into account in a fitting model. The refractive index was measured to be 3.82 at 200 nm and continuously decreased to 2.52 as the wavelength approached 1600 nm. The value measured at wavelengths less than 250 nm was slightly smaller than that of 4H-SiC reported elsewhere.21 The measured refractive index at wavelengths greater than 250 nm agreed well with data in the existing literature.21 The extinction coefficient was measured to be 1.66 at 200 nm and continuously decreased at larger wavelengths. Our experimental extinction coefficient agrees well with that of the past literature, except for the wavelength near 200 nm.18 The measured extinction coefficient (i.e., 1.66 at 200 nm) was three times larger than that (i.e., 0.55) of the literature.21 It was reported that the optical constants of semiconductors could be modified by ion implantation. The smaller refractive index and larger extinction coefficient at wavelengths smaller than 250 nm are ascribed to structural defects associated with H+ ion implantation.22 In addition, our larger extinction coefficient could be further explained by a Fabry–Perot effect due to reflection between the two surfaces of the SiC NM. Fig. 5(c) shows the absorption coefficient (\(a\)) of the SiC layer calculated using the equation:

\[
\alpha = (4 \times \pi \times k) / \lambda 
\]

where \(\alpha\) is the absorption coefficient, \(k\) is the extinction coefficient, and \(\lambda\) is the wavelength. Based on the measured extinction coefficient, the absorption coefficients of the SiC layer were calculated to be 9500 and 4830 cm\(^{-1}\) at 320 and 350 nm, respectively. They are approximately 6 and 10 times greater than those of the reported values (i.e., 1550 and 420 cm\(^{-1}\) at 320 and 350 nm, respectively).23,24 Although no experimental data on the absorption coefficients of 4H-SiC have been reported at wavelengths shorter than 300 nm, our absorption coefficient is expected to be larger in the 200–300 nm range, which can be confirmed from the measured absorption below.

To further characterize the light absorption of the SiC NM, reflection and transmission spectra were measured on SU-8/PET and SiC NM/SU-8/PET stacks, respectively. Fig. 5(d) and (e) show...
transmission, reflection, and absorption spectra of the SU-8/PET and SiC NM/SU-8/PET stacks. The reflection ($R$) was measured to be approximately 15% on average in the wavelength range of 200–500 nm. A sharp increase in the transmission ($T$) was observed at 315 nm and approached 80% at wavelengths larger than 375 nm. In contrast, the absorption ($A$) sharply decreased to nearly zero beyond 400 nm. A similar trend to the SU-8/PET stack was also observed in the SiC NM/SU-8/PET stack except for an increased reflection, which leads to decreased absorption and transmission in their respective wavelength ranges. Based on the measured data, the absorption of the SiC NM can be derived using the following equation:

$$A_{\text{SiC NM}} = 1 - R_{\text{SiC NM/SU-8/PET}} - T_{\text{SiC NM/SU-8/PET}} - T_{\text{SiC NM}} \times A_{\text{SU-8/PET}}$$ (2)

where $T_{\text{SiC NM}}$ is the light that reaches the interface of the SiC NM and SU-8/PET. This term should be incorporated in eqn (2) to subtract the absorption of the SU-8/PET stack. Fig. 5(f) shows the absorption spectrum of the SiC NM obtained using eqn (2) in the wavelength range of 200–500 nm. The absorption decreased from 73.8% at 256 nm to about 5% at 360 nm. The oscillations with multiple peaks in the measured absorption spectrum in Fig. 5(f) can be ascribed to the Fabry–Perot effect due to the finite thickness of the SiC NM. The absorption of the SiC NM was also calculated numerically using the following equations:25

$$r = \left[\left(n - 1\right)^2 + k^2\right]/\left[\left(n + 1\right)^2 + k^2\right]$$ (3)

$$A = \left[\left(1 - r\right)/(1 - e^{-at})\right]/\left(1 - re^{-at}\right)$$ (4)

where $n$ is the refractive index, $k$ is the extinction coefficient, $a$ is the absorption coefficient, and $t$ is the thickness of the SiC NM. It should be noted that all parameters used in eqn (3) and (4) are measured results. Comparison between the experimental and calculated absorption spectra shows qualitative agreement as shown in Fig. 5(f). The difference may be ascribed to the error from measured optical constants and properties of the SiC NM. The high absorption (i.e., greater than 40%) of the SiC NM in the 200–260 nm wavelength range led to a shallow penetration depth in the SiC NM. The penetration depths were calculated to be 10 and 157 nm at wavelengths 200 and 260 nm, respectively.24

In order to show the reliable flexibility of the SiC NM, we performed a series of bending tests. The SiC NM/SU-8/PET samples were bent on bending fixtures with radii of 77.5, 38.5, and 21 mm. No cracks or wrinkles were observed in all the samples. We also measured the reflection, absorption, and transmission spectra of the samples after bending. No change in the absorption spectrum of the SiC NM clearly indicated the SiC NM to be flexible and applicable for flexible UV photodetectors.

3. Conclusions

In summary, we have demonstrated a transferable single crystalline 4H-SiC NM. The SiCOI source wafer was fabricated using the Smart-Cut® technique and the released SiC NM was successfully transferred onto the PET substrate. Good crystallinity and a smooth surface were realized after transfer of the SiC NM. The optical properties of the SiC NM were studied, which revealed an absorption of 73.8% at 256 nm and an average absorption of 57% in the wavelength range of 200–260 nm. The results suggest that our transferrable SiC NM is readily applicable for high performance flexible UV photodetectors.

4. Experimental

Fabrication of the SiCOI wafer

Fig. 1 shows a schematic process flow used to fabricate the 4H-SiCOI wafer. The process began with a thorough cleaning of a semi-insulating SiC wafer (Cree, Inc., resistivity: $> 1 \times 10^5 \Omega$ cm) with acetone, IPA, and DI water. A 100 nm thick plasma enhanced chemical vapor deposition (PECVD) SiO$_2$ layer was deposited on the 2 inch 4H-SiC wafer as a screen oxide to obtain a uniform ion implantation profile (Fig. 1(i)). The oxide-capped SiC wafer was implanted with H$^+$ ions at a dose of $8 \times 10^{16}$ cm$^{-2}$ and an energy of 130 keV to place the peak position of an H$^+$ implantation profile at 800 nm from the SiC surface (Fig. 1(ii)). A 300 nm thick SiO$_2$ layer was thermally grown on a Si handling substrate to form the buried oxide (BOX) layer of the final structure of the SiCOI wafer (Fig. 1(iii)). After performing H$^+$ ion implantation, the screen oxide was completely removed from the SiC wafer by hydrofluoric acid (HF, 49%). The implanted SiC wafer was diced into pieces of size 1.5 x 1.5 cm$^2$ to perform a series of annealing experiments (e.g., at annealing temperatures of 850, 950, and 1050 °C) for a complete exfoliation of the SiC layer. The diced SiC piece was manually bonded to the oxidized Si substrate at room temperature (Fig. 1(iv)). No annealing process was applied for initial bonding. The bonded wafer was directly loaded into a tube of the MRL Atmospheric Furnace at an idle temperature of 380 °C. Careful temperature control was applied with a ramp up and down of 4 and 2 °C min$^{-1}$, respectively, to avoid thermal shock. The bonded wafers were annealed at different temperatures (i.e., 850, 950, and 1050 °C) for 8 hours in a nitrogen atmosphere (Fig. 1(v)). The surface of the transferred SiC layer was rough after the complete exfoliation of the SiC layer due to blisters. In addition, the top region of the transferred SiC layer was highly damaged by the H$^+$ ion implantation.26 In general, a damage-free layer with smooth surface roughness is achieved by chemical mechanical planarization (CMP) after the Smart-Cut® process. However, CMP is not a viable method to polish the SiC layer of the SiCOI wafer due to its relatively slow material removal rate (MRR) which is attributed to the hardness of SiC (i.e., 2800 kg mm$^{-2}$).27,28 In order to achieve a damage-free SiC layer with a smooth surface roughness, the inductively coupled plasma (ICP) etcher (PT770-ICP) with a gas mixture of boron chloride (BCl$_3$), chlorine (Cl$_2$), and argon (Ar) was used (Fig. 1(iv)). The as-split SiC layer was etched with two gas mixtures of 10/15/3 and 20/15/3 sccm for BCl$_3$/Cl$_2$/Ar, respectively, with the same ICP and RIE power of 250 W and 300 W at 2 mTorr chamber pressure.
Transfer of the SiC NMs on flexible substrates

The top SiC template layer was released from the SiCOI wafer and subsequently transferred onto a 180 μm thick polyethylene terephthalate (PET) substrate coated with a 1 μm thick adhesive layer (MicroChem, SU-8 2002). The SiC NM transfer process consisted of patterning the top SiC layer and releasing the SiC NM from the SiCOI wafer. The NM pattern (size: 3 × 3 mm²) with an array of etching holes (size: 3 × 3 μm²) that were 50 μm apart was formed on the SiC layer by photolithography. The SiC layer outside the pattern was completely removed by the ICP etcher to expose the bottom oxide layer, removed by immersing in 49% aqueous HF for 1 hour. The SiC NM settled down on the Si handling substrate via van der Waals forces (Fig. 1(v)). The freestanding SiC NM was gently picked up by an elastomeric polydimethylsiloxane (PDMS) stamp and transferred onto the PET film (Fig. 1[vi]–(viii)).

Material characterization of the SiC NM

The surface roughness of the as-split and as-etched SiC layers in the SiCOI wafer was carefully measured by AFM (Bruker BioScope Catalyst AFM). XPS (Thermo Scientific K-Alpha XPS) was performed on the as-split and as-etched SiC layers of the SiCOI wafer. In addition, the crystal quality of the SiC NM was analyzed by using HR-XRD (PAAnalytical X’Pert PRO X-ray diffractometer). Optical constants (i.e., refractive index and extinction coefficient) of the SiC layer of the SiCOI wafer were investigated by using an ellipsometer (J. A. Woollam M-2000 DI) in the wavelength range of 200–1600 nm.

Optical characterization of the SiC NM

The SiC NM reflection and transmission were measured using a custom-built reflection and transmission system at room temperature. The samples were characterized using a monochromator (Horiba-iHR550)-based setup with a UV light source (DH-2000-S-DUV). The light was incident from the surface normal direction on the sample by passing a deep UV enhanced beam splitter and glass lens (f = 75 mm). The spot size was set to ~2 mm by an aperture, which is smaller than the area of the SiC NM. The reflected and transmitted light were guided into the monochromator and detected with a thermoelectrically cooled CCD detector. The reflectivity was obtained by normalizing with the reflection spectrum measured from the calibrated Al reference mirror (Edmund Optics) with measured reflectivity of 92% over the spectral range of 200 to 500 nm. The transmission was estimated by normalizing with the light intensity through the free space. The absorption was obtained by using the equation: \( A = 1 - R - T \). The estimated measurement error was around 1–2%, which is mainly associated with the real reflectivity of the reference Al mirror.

Notes and references