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ABSTRACT

Self-assembled molecular monolayer doping is an emerging doping technique. In this work, we investigated the activation rate and photoresponses of boron doped silicon by self-assembled molecular monolayer doping. By using low temperature Hall effect measurements and by secondary ion mass spectroscopy, we find that the activation rate of boron in these samples is in the range of 91%–54%, depending on the doping concentration. Interestingly, the photoresponsivity of the boron doped samples is also significantly higher than that of the phosphorus doped samples even though the same doping technique is used. The intriguing photoresponses are closely related to the trapping of photogenerated minority carriers by the defects in the p-type silicon.

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INTRODUCTION

Monolayer doping (MLD) is an emerging technique for controlled doping at nanoscale. Compared with ion implantation, MLD creates no lattice damage and is capable of forming conformal doping for 3-dimensional field effect transistors. In MLD, the dopant molecules are first immobilized on a cleaned wafer surface. During that process, the concentration of the dopants can be tuned by changing the reaction conditions, such as temperature, time, or the composition ratio of the dopant. Ho et al. were the first to fabricate boron doped silicon by monolayer doping. Ye et al. controlled the dopant dose by the method of mixing the dopant-containing alkenes and nondopant-containing alkenes. We previously showed that the defects of interstitial carbon and substitutional phosphorus pairs (C_i-P_s) can electrically deactivate phosphorus dopants with an activation rate of ~80%. At low concentration, the activation rate of phosphorus dopants introduced by molecular monolayer doping is surprisingly as low as 7%.

In this work, we investigated the dopant activation and photoresponses of silicon samples doped via self-assembled molecular monolayer doping. The activation rate of boron dopants was found to be in the range of 91%–54%, depending on the doping concentration. Interestingly, when the samples were under illumination, these boron-doped samples show photoresponse orders of magnitude higher than the blank silicon sample and phosphorus doped samples by MLD doping. This is because the defects in the p-type silicon (boron doped) are unfilled and have a high chance to capture photogenerated minority electrons, inducing a strong photoresponse.

RESULTS AND DISCUSSION

Silicon-on-insulator (SOI) wafers were first cleaned with piranha [H_2SO_4:H_2O_2 = 3:1 (v:v)] and subsequently etched with HF solution to remove the native silicon oxide, forming H-terminated silicon surfaces [Fig. 1(a)]. The cleaned silicon surface reacted with the allylboronic acid pinacol ester (ABAPE) in 1, 3, 5-mesitylene solution at a temperature of 160 °C for 48 h [Fig. 1(b)]. After high temperature thermal annealing at 1050 °C for 5 min, the B dopants were driven into the silicon device layer of the SOI wafer [Fig. 1(c)].
FIG. 1. Fabrication process of monolayer doped samples: (a) native SiO$_2$ on the SOI wafer is etched by dilute aqueous HF, yielding a H-terminated silicon surface, (b) the dopant molecules are chemically grafted onto the H-terminated silicon surface, and (c) the dopants are driven into silicon by high temperature thermal annealing.

The doped sample was labeled Sample 1. The experimental processes were repeated to obtain low concentration boron-doped samples (Sample 2) by mixing 1-undecene with ABAPE at a mole ratio of $\sim$1:1 to dilute the surface concentration of ABAPE molecules grafted on silicon surfaces.

The surface modified samples were characterized by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 2. A strong B 1s peak at 191.1 eV is clearly visible at the left shoulder of the broad silicon plasma peak [Fig. 2(a)]. The C-C and C-O peaks were detected as shown in Fig. 2(b). The ratio of the C-C and C-O peak area is $\sim$3.2:1, which is close to the stoichiometric ratio of the ABAPE (C$_9$H$_{17}$O$_2$B) molecules. These results indicate that the ABAPE molecules have been successfully grafted on the silicon surfaces.

To investigate the activation rate of boron doping at different concentrations, we coated the surface modified samples with a thin layer of 200 nm thick SiO$_2$ by spin-coating with spin-on-glass (SOG, Futurrex, Inc., USA). The samples were then annealed at 1050 °C for 5 min. After annealing, the samples were dipped in HF solutions (5%) for 10 min to remove the SOG capping layer. The four corners of the silicon samples were in contact with Al pads formed by thermal evaporation. Van der Pauw measurements were performed in darkness. The sheet resistances are summarized in Table I. A control sample went through all the processes with other doped samples except the self-assembly of ABAPE. The sheet resistance of the control sample is as high as 2158.8 kΩ/sq, indicating that the contamination in the processes is negligible. The ABAPE-doped samples have a sheet resistance of 6.7 kΩ/sq and 28.2 kΩ/sq for the samples with high-doping concentration (Sample 1) and low-doping concentration (Sample 2), respectively. Clearly, it shows that boron dopants have been successfully diffused into the silicon substrate. The sheet resistance of Sample 2 is unexpectedly more than 4 times larger than that of Sample 1 although the concentration of ABAPE molecules is only half diluted by mixing 1-undecene with ABAPE at a mole ratio of $\sim$1:1. This is mainly caused by the lower ionization of boron dopants in Sample 2, which will be discussed in detail.

Low temperature Hall measurements were performed on the boron doped samples. The Hall resistance is linear to the magnetic field (insets of Fig. 3) and is based on the following equation,
TABLE I. Sheet resistances of monolayer doping samples by van der Pauw measurements.

| SOI wafer, resistivity >10 k Ω cm | Rs (kΩ/sq) |
|-----------------------------------|------------|
| Control sample                    | 2158.8     |
| Sample 1 (high-doping concentration) | 6.7        |
| Sample 2 (low-doping concentration) | 28.2       |

from which the hole concentration can be found,

\[ p = -\frac{\Delta B}{e \times \left(\Delta V_H/I\right)} \]

where \( p \) is the hole concentration per unit area, \( e \) is the unit charge, \( B \) is the magnetic field intensity, \( V_H \) is the Hall voltage, and \( I \) is the source current.

The hole concentration per unit area can be found as the temperature is lowered from 300 K to 80 K, as shown in Fig. 3. Theoretically, the hole concentration per unit area \( p \) is correlated with the temperature and activation energy as given in the following equation:

\[ p = \frac{-w(kT)^{\frac{3}{2}} \times \left(-1 + \sqrt{1 + \frac{16N_A\exp\left(\frac{E_A}{kT}\right)}{w(kT)^{\frac{3}{2}}} \right)}}{8\exp\left(\frac{E_A}{kT}\right)} \]

Equation (2) can be fitted to the experimental data in Fig. 3, from which we found the activation energy level \( E_A \) is located at 41–42 meV above the valence band, which is consistent with the ionization energy level of boron dopants in silicon. The concentration of electrically active boron dopants in silicon is \( 7.15 \times 10^{12} \text{ cm}^{-2} \) (Sample 1) and \( 1.81 \times 10^{12} \text{ cm}^{-2} \) (Sample 2).

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Secondary ion mass spectroscopy (SIMS) was performed to probe the boron doping profile in silicon, as shown in Fig. 4. The total number of dopants is \( 7.82 \times 10^{12} \text{ cm}^{-2} \) and \( 3.34 \times 10^{12} \text{ cm}^{-2} \) for Sample 1 (black dots) and Sample 2 (red dots), respectively. This is consistent with the fact that the ABAPE molecules grafted on Sample 2 was diluted by mixing 1-undecene with ABAPE at a mole ratio of ∼1:1. Considering that the concentrations of electrically active dopants were previously found from low temperature Hall measurements, the activation rate of dopants can be calculated as 91.4% and 54.2% for Sample 1 and Sample 2, respectively.

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FIG. 5. (a) Photocurrent of different samples and (b) photoresponsivity of high concentration boron-doped sample changes with illumination time and with a wavelength of 532 nm and 7.2 mW cm⁻², respectively.

The boron dopants that are electrically inactive are likely caused by the deactivation effect of defects. Previous work indicated that boron can bind with carbon, forming B-C complexes that have energy levels located in the upper half bandgap. Indeed, a high concentration of carbon impurities diffused into silicon along with boron dopants (inset in Fig. 4). For a p-type silicon, defects in the upper half bandgap are empty and will capture photogenerated minority electrons. The corresponding excess holes will accumulate in the valence band, inducing high photoresponsivity. A higher concentration of defects in the upper half bandgap will lead to large photoresponsivity. To verify this observation, we illuminated the ABAPE doped silicon with light at a wavelength of 532 nm. To avoid the effect of surface states on photoresponsivity, 200 nm SiO₂ was deposited on the surface of all samples under investigation by atomic layer deposition (ALD). The starting silicon wafers are all intrinsic with a resistivity higher than 10 000 Ω cm. As shown in Fig. 5, the photoresponsivity of the intrinsic wafer is ~0.7 mA/W when the applied electric field intensity in the wafer is not more than 2 V/cm. After the wafers were doped with ABAPE monolayers, the photoresponsivity is increased by 2–3 orders of magnitude at the same applied electric field intensity. As the boron doping concentration increases, the photoresponsivity becomes higher.

The correlation of boron doping concentration and photoresponses indicates that the defects are boron-correlated ones, mostly B-C complexes, as indicated by previous results. For comparison, we also investigated the photoresponses of silicon wafers that were doped with octadecylphosphonic acid (ODPA) monolayers. The P-doped silicon is an n-type. SIMS data show that the P doping concentration is ~2.99 × 10¹² cm⁻², which is close to the B doping concentration in Sample 2. Our previous work indicates that the activation rate of phosphorus dopants at a similar doping concentration is as low as 7%. It implies that phosphorus-related defects (mostly C₁₋P defects) are higher in concentration than boron-related defects in Sample 2. Surprisingly, the photoresponsivity of the phosphorus doped sample is about one order of magnitude lower than Sample 2. This surprising observation is caused by the fact that the defects of C-P binding pairs are located in the upper half bandgap in silicon. For n-type doping semiconductors, the carbon-related defects are filled with majority electrons. The chances that photogenerated electrons and holes are captured by these defects are low. As a result, the ODPA doped silicon is not highly photoresponsive.

CONCLUSION
We fabricated boron-doped silicon samples with different doping concentrations by molecular monolayer doping. The activation rate of boron in these samples is generally higher than that in the phosphorus doped samples by molecular monolayer doping. It is likely because the defect concentration in boron-doped samples is relatively low. However, a lower concentration of defects in boron-doped samples induces higher photoresponsivity since these defects are empty in the p-type silicon and have a high chance to capture photogenerated minority electrons.

EXPERIMENTAL
Materials
FZ SOI wafers with the following specifications were purchased from Suzhou Resemi Semiconductor Co., Ltd.: (100)-oriented, 10 ± 1 μm thick top silicon layer, 1 μm thick buried oxide, 600 ± 10 μm thick silicon base, and >10 kΩ cm resistivity. Acetone and ethanol are of CMOS grade (Sinopsin Group Chemical Reagent Co., Ltd.). Allylboronic acid pinacol ester (ABAPE) (97%) and hydrofluoric acid (HF, 48%, CMOS grade) were from Sigma Aldrich. H₂SO₄ (98.08%) and H₂O₂ (30%) were bought from Sinopsin Group Chemical Reagent Co., Ltd. 1-undecene (98%) and 1, 3, 5-mesitylene (97%) were from Aladdin.
Monolayer formation

SOI wafers are cut into pieces of little squares (1 cm × 1 cm). Then, the squares are cleaned by acetone and ethanol for 3 min in an ultrasonic cleaner. Washed by DI water, the square samples are blown dry with N₂. The wafers are immersed in piranha solution (H₂SO₄:H₂O₃ = 3:1) for 40 min on a hot plate at a temperature of 120 °C. Next, 2.5% HF solution is used to etch the oxide layer formed because of the reactions mentioned in the previous steps, forming a hydrogen-terminated silicon surface. After quick washing by deionized (DI) water and drying with N₂, the square samples are immersed in a reaction solution for monolayer doping in a glovebox (Universal, Mikrouna) for 48 h at 160 °C. For high concentration boron-doped samples, the reaction solution consists of 1 ml ABAPE and 10 ml 1, 3, 5-mesitylene, and for low concentration boron-doped samples, the solution consists of 0.5 ml ABAPE and 0.5 ml 1-undecene.

Silicon dioxide deposition and thermal annealing

The wafers are transferred from the reaction solution to acetone and ethanol in an ultrasonic cleaner for 3 min to remove the absorbent solution. After DI water washing and N₂ tone and ethanol in an ultrasonic cleaner for 3 min to remove formed because of the reactions mentioned in the previous steps, the square samples are baked at 100 °C for 1 min and then at 200 °C for 2 min. The wafers are transferred to a thermal annealing furnace (Thermo Scientific Lindberg/Blue, USA) at 400 °C for 30 min and then at 1050 °C for 5 min. The boron-doped silicon samples are immersed in a buffer oxide etchant (BOE), consisting of HF and NH₄F at the ratio 6:1, to remove the SiO₂ capping layer on the surface.

XPS

XPS is performed on a Kratos AXIS Ultra DLD spectrometer system with an Al source. The takeoff angle is 45°. The vacuum degree in the analysis chamber is about 10⁻⁶ Torr. The energy of the survey scan and narrow scan are 160 eV and 40 eV with the same power of 105 W.

van der Pauw measurement

The metal electrodes at the four corners of the silicon surface for electrical measurement are fabricated by evaporating 20 nm cobalt film and 200 nm aluminum film in a thermal evaporation system (Angstrom Engineering, Canada). Sheet resistance is obtained by four probe measurements on a probe station with four probes in contact with the four metal electrodes in darkness. Voltage and current are applied, and the data is collected by using Keithley 2400 source meter units according to the specific Labview script. For photoresponsivity measurements, the samples are under uniform laser illumination with a wavelength of 532 nm.

Hall measurement

The electrodes are connected to the sample holder by wire bonding. For the square wafers, the current is applied along the diagonal of the surface, and the magnetic field is perpendicular to the current and surface. According to the Hall effect, a transverse electric field and potential difference are generated, which are perpendicular to both the current and the magnetic field. The measurement is performed using a physical property measurement system (PPMS, Quantum Design, USA) at about 17.26 Torr. The data are collected by Keithley 2400 source meter units according to the specific Labview script.

SIMS

The boron SIMS profiling is performed at EAG Laboratories using Adept 1010 and with a Cs⁺ primary ion, negative secondary polarity, primary voltage of 5 k eV, raster of 300 µm, instrument vacuum of 10⁻¹⁰ Torr.

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REFERENCES

1. K. Cho et al., “Molecular monolayers for conformal, nanoscale doping of InP nanopillar photovoltaics,” Appl. Phys. Lett. 98, 203101 (2011).
2. G. Collins and J. D. Holmes, “Chemical functionalisation of silicon and germanium nanowires,” J. Mater. Chem. 21, 11052–11069 (2011).
3. R. C. Longo, K. Cho, W. G. Schmidt, Y. J. Chabal, and P. Thissen, “Monolayer doping via phosphonic acid grafting on silicon: Microscopic insight from infrared spectroscopy and density functional theory calculations,” Adv. Funct. Mater. 23, 3471–3477 (2013).
4. S. Caccamo et al., “Silicon doped by molecular doping technique: Role of the surface layers of doped Si on the electrical characteristics,” Mater. Sci. Semicond. Process. 42, 200–203 (2016).
5. E. Y.-J. Kong, P. Guo, X. Gong, B. Liu, and Y.-C. Yeo, “Toward conformal damage-free doping with abrupt ultrashallow junction: Formation of Si monolayer and laser anneal as a novel doping technique for InGaAs nMOSFETS,” IEEE Trans. Electron Devices 61, 1039–1046 (2014).
6. K.-W. Ang et al., in Proceedings of 2011 IEEE International Electron Devices Meeting (IEDM) (IEEE, Washington, DC, USA, 2011).
7. E. Arduca et al., “Synthesis and characterization of P 5-layer in SiO₂ by monolayer doping,” Nanotechnology 27, 075606 (2016).
8. B. Long et al., in Proceedings of 20th International Conference on Ion Implantation Technology (IIT) (IEEE, Portland, OR, USA, 2014).
9. J. C. Ho, R. Yerushalmi, Z. A. Jacobson, Z. Fan, R. L. Alley, and A. Javey, “Controlled nanoscale doping of semiconductors via molecular monolayers,” Nat. Mater. 7, 62 (2018).
10. J. C. Ho, R. Yerushalmi, G. Smith, and P. Majhi, “Wafer-scale, sub-5 nm junction formation by monolayer doping and conventional spike annealing,” Nano Lett. 9, 725–730 (2009).
11. L. Ye, S. P. Pujari, H. Zuilhof, T. Kudernac, M. P. de Jong, W. G. van der Wiel, and J. Husken, “Controlling the dopant dose in silicon by mixed-monolayer doping,” ACS Appl. Mater. Interfaces 7, 3231 (2015).
12. X. Gao, B. Guan, A. Meši et al., “Deep level transient spectroscopic investigation of phosphorus-doped silicon by self-assembled molecular monolayers,” Nat. Commun. 9, 118 (2018).
13. H. Wu, B. Guan, Y. Sun et al., “Controlled doping by self-assembled dendrimer-like macromolecules,” Sci. Rep. 7, 41299 (2017).
14. B. Guan, H. Siampour, Z. Fan et al., “Nanoscale nitrogen doping in silicon by self-assembled monolayers,” Sci. Rep. 5, 12641 (2015).

15. E. V. Monakhov, A. Nylandsted Larsen, and P. Kringhøj, “Electronic defect levels in relaxed, epitaxial p-type Si1-xGex layers produced by Mev proton irradiation,” J. Appl. Phys. 81, 1180 (1997).

16. Y. Dan, X. Zhao, K. Chen, and A. Mesli, “A photoconductor intrinsically has no gain,” ACS Photonics 5, 4111–4116 (2018).

17. K. Chen, X. Zhao, A. Mesli, Y. He, and Y. Dan, “Dynamics of charge carriers in silicon nanowire photoconductors revealed by photo Hall effect measurements,” ACS Nano 12, 3436–3441 (2018).