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Monolayer Contact Doping from a Silicon Oxide Source Substrate

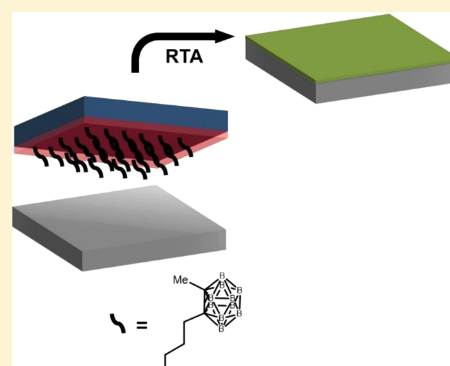
Liang Ye,[†,‡] Arántzazu González-Campo,[§] Tibor Kudernac,[†] Rosario Núñez,[∥] Michel de Jong,[‡] Wilfred G. van der Wiel,[‡] and Jurriaan Huskens*,[†]

[†]Molecular NanoFabrication and [‡]NanoElectronics groups, MESA+ Institute for Nanotechnology, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

[§]Functional Nanomaterials and Surfaces and [∥]Inorganic Materials and Catalysis groups, Institut de Ciència de Materials de Barcelona (ICMAB-CSIC), Campus de la UAB, 08193, Bellaterra, Spain

Supporting Information

ABSTRACT: Monolayer contact doping (MLCD) is a modification of the monolayer doping (MLD) technique that involves monolayer formation of a dopant-containing adsorbate on a source substrate. This source substrate is subsequently brought into contact with the target substrate, upon which the dopant is driven into the target substrate by thermal annealing. Here, we report a modified MLCD process, in which we replace the commonly used Si source substrate by a thermally oxidized substrate with a 100 nm thick silicon oxide layer, functionalized with a monolayer of a dopant-containing silane. The thermal oxide potentially provides a better capping effect and effectively prevents the dopants from diffusing back into the source substrate. The use of easily accessible and processable silane monolayers provides access to a general and modifiable process for the introduction of dopants on the source substrate. As a proof of concept, a boron-rich carboranyl-alkoxysilane was used here to construct the monolayer that delivers the dopant, to boost the doping level in the target substrate. X-ray photoelectron spectroscopy (XPS) showed a successful grafting of the dopant adsorbate onto the SiO_2 surface. The achieved doping levels after thermal annealing were similar to the doping levels accessible by MLD as demonstrated by secondary ion mass spectrometry measurements. The method shows good prospects, e.g. for use in the doping of Si nanostructures.



INTRODUCTION

The doping of silicon plays a crucial role in tuning the properties of electronic devices. The ever evolving technology in semiconductor industry drives devices to smaller dimensions in order to achieve higher performance and to reduce the costs of their production.[1,2] In this downscaling trend, realizing shallower doping while preventing crystal damage becomes a key prerequisite.[3] Monolayer doping (MLD) is promising as an alternative technique for forming doped structures in silicon.[4−7] It utilizes a reaction known as hydrosilylation[8] to covalently bind dopant-containing alkene molecules onto the silicon surface of the target wafer. The dopant is then driven into the silicon through rapid high-temperature annealing. Covalent anchoring of alkenes on silicon via hydrosilylation requires the utilization of a hydrogen-terminated silicon surface, which is achieved by removing the native oxide layer by wet fluoride etching.[8,9] Other covalent bonding mechanisms have been used subsequently to attach dopant molecules onto different substrates such as Ge,[10] InGaAs,[11] and SiO_2[12,13] surfaces. Moreover, MLD employs a capping layer of SiO_2 that is deposited on the monolayer prior to the thermal annealing step, which is required to prevent the dopant from escaping from the target surface during the annealing process. This capping layer needs to be removed after the drive-in process again by fluoride etching. These fabrication steps can be incompatible with the substrate, especially when aiming for devices that are fabricated on silicon-on-insolator (SOI) wafers. Removal of the capping layer can cause the backside oxide layer to be removed as well.

Yerushalmi and co-workers have proposed monolayer contact doping (MLCD), which solves the materials incompatibility issue.[14] MLCD features a dopant monolayer formed on a separate silicon substrate, which functions as the source substrate. This source substrate is brought into contact with the target substrate that needs to be doped. In a thermal annealing step, the dopant is driven into the target substrate. The source substrate is then discarded, leaving the doped layer on the target substrate. Following this approach, the target substrate does not have to undergo any wet chemistry and postdoping processing. Higher levels of doping can, in principle, be achieved by repeating the MLCD process using multiple source substrates on a single target substrate. Moreover, it has been demonstrated that the doping of 3D structures (e.g., Si nanowires)[14] can be achieved using this technique.

MLCD and the use of a separate silicon oxide source substrate provides a series of potential advantages: (i) avoiding

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the use of a capping layer, (ii) thereby avoiding contact of solvents with the target substrate, (iii) reduced dopant diffusion into the source substrate when a sufficiently thick silicon oxide substrate is used, allowing more efficient uptake by the target substrate, and (iv) the use of monolayers of molecules that bind to silicon oxide at the surface of the source substrate, of which silanes are the most common. The important advantages (i) and (ii) have been covered in the seminal work of Yerushalmi and co-workers.[14] Point (iii), however, has not been investigated in depth, because, so far, only silicon substrates with a thin (few nm) native silicon oxide layer have been used as the source substrate, although this native oxide has already been shown convincingly to result in improved sheet resistances compared to the use of Si substrates with adsorbates bound to H−Si.[14] The use of a thick oxide layer could further reduce the diffusion of dopants into the source substrate. Regarding the type of monolayer chemistry that is used on silicon oxide (issue (iv)), the work of Yerushalmi described the use of phosphine oxides as P-doping adsorbates resulting in P−O−Si bond formation,[14] while others have used direct B−O−Si bond formation to introduce B dopants.[12] Remarkably, the most well-known monolayer chemistry for silicon oxide, i.e., the use of silanes, has not been described in MLCD so far. Arguably, silane monolayers can be more deterministic and used for a wider range of dopants, as they avoid the direct binding of the desired dopant atom to the silicon oxide surface. For example, methods to control the dopant layer by using mixed monolayers[15] are only useful when both adsorbates have a similar reactivity, something that cannot be achieved when the dopant constitutes the reactive headgroup.

Here, we propose MLCD with the use of a 100 nm thick thermal SiO_2 layer (on Si) subsequently functionalized with an alkoxysilane monolayer as the source substrate. The SiO_2 source substrate used here acts at the same time as a capping layer, thus preventing the loss of dopant atoms by diffusion into the source substrate. Furthermore, we use a boron-rich carborane silane derivative to boost the doping level in the target substrate. Contact angle, X-ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy, and resistance measurements were performed to study the monolayer on the source substrate, and to explore the process of doping by this modified MLCD process.

■ RESULTS AND DISCUSSION

The proposed monolayer contact doping process is schematically shown in Figure 1, and employs the carboranyl-alkoxysilane derivative, 1-(CH_3)-3-$CH_2CH_2CH_2Si$-$(OCH_2CH_3)_3$-1,2-closo-$C_2B_{10}H_{10}$ (see Supporting Information). The monolayer grafting onto the SiO_2 source substrate was accomplished by using a 1% v/v solution of the carboranyl-alkoxysilane in dry toluene at room temperature overnight. The dopant was transferred into the target substrate by bringing the source substrate into contact with the target substrate and annealing them at 1000 °C using rapid thermal annealing (RTA).

The formation of the silane monolayer on the source substrate was initially evidenced by contact angle (CA) measurements. After cleaning, the starting oxide-coated substrate was highly wetted (CA < 20°). After monolayer formation, the CA had increased to 81.8°. The CA of the same sample after three-week storage in air was 81.5°, which indicates that the monolayer is stable for at least 3 weeks under ambient conditions. Upon RTA, the monolayer was decomposed, and the dopant atoms were driven into the target substrate. This was accompanied by a dramatic decrease of the contact angle of the source substrate down to 7.1°.

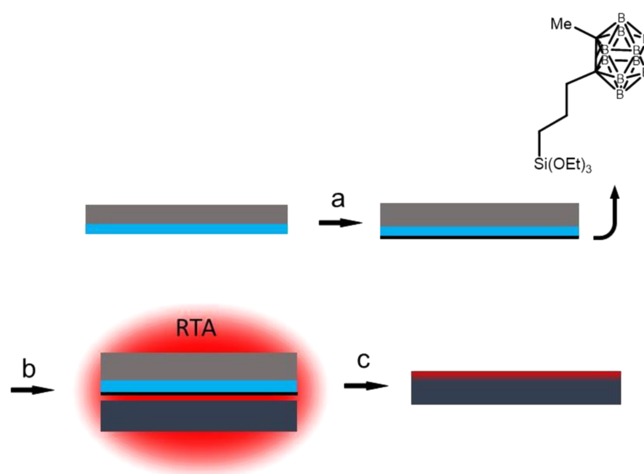

Figure 1. Monolayer contact doping process using a silicon oxide source substrate. A silicon wafer (gray) with a 100 nm layer of thermal SiO_2 (blue) is used as the source substrate, and (a) is functionalized with a monolayer of a carboranyl-alkoxysilane. (b) The source substrate is brought into contact with the target silicon substrate (dark gray), and both are loaded into a thermal furnace for rapid thermal annealing (RTA). (c) The dopants are driven into the target substrate forming a doped surface layer (red).

XPS was performed on the source substrate right after the monolayer formation as well as after a 3-week storage in air. The boron signals at 189.7 eV attributed to the B−H of the carborane clusters are shown for both substrates in Figure 2.

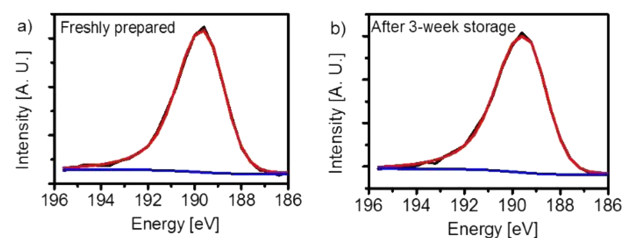

Figure 2. XPS measurements on SiO_2-covered Si wafer pieces with carboranyl-alkoxysilane monolayers showing the boron signal at 189.7 eV for samples (a) right after the monolayer formation and (b) after three-week storage in air.

Quantitative measurements of the elements B, C, O, and Si are summarized in Table 1. The XPS data reported before of allyl-carborane clusters on silicon surface for MLD is also shown in the table for comparison.[16] The amount of boron on the samples (7.26%) is of the same order of magnitude as obtained for a monolayer of an alkene-functionalized carborane on H-terminated silicon (9.33%) that was used in MLD. This

Table 1. Elemental Composition of Carboranyl-Alkoxysilane Monolayers on Oxide-Covered Si Substrates Measured by XPS

	B [at. %]	C [at. %]	O [at. %]	Si [at. %]
freshly prepared	7.26	16.28	52.61	23.86
3-week storage in ambient	6.27	11.58	56.53	25.63
CB-(Me, allyl)[13]	9.33	29.31	19.65	41.72

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indicates a similar amount of boron is present on the surface of the MLCD source substrate. The amount of boron on the surface after three-weeks storage was found to be at a similar level (6.27%) as the freshly prepared surface. The B-to-C ratios were higher for the silane monolayers than for the alkene monolayer, indicating less adsorption of adventitious carbon.

After the monolayer formation, the source substrate was brought into contact with a target Si wafer substrate upon which the substrate stack was annealed at 1000 °C for 6 s in an RTA process to drive the dopant into the target substrate. A single source substrate was used to dope three intrinsic silicon target substrates (samples 1, 2, and 3) consecutively (without refilling it) to monitor the depletion of boron from the source. The sheet resistance (R_s) of these targets was subsequently measured (Figure 3).

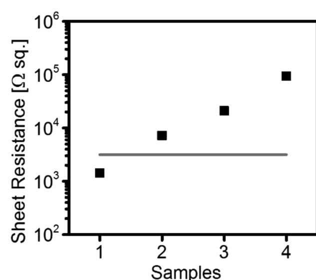

Figure 3. Sheet resistance (R_s) measurements of intrinsic silicon samples that were consecutively doped by a single SiO_2 source substrate functionalized with a monolayer of a carboranyl-alkoxysilane (samples 1 to 3) and of an intrinsic wafer that received no doping (4). The gray line indicates the R_s measured on an intrinsic silicon surface that was doped using MLD with a carborane alkene and reported previously.[15] Errors of the measurements were found to be less than 7% on any of the data points shown here.

Comparing the R_s of the target doped by MLCD (sample 1) to the ones achieved from MLD using carborane alkene derivatives on H-terminated silicon (gray line in Figure 3, reported by us previously[16]), they are of the same order of magnitude, and both are 2 orders of magnitude lower than the resistance of the intrinsic silicon substrate before doping (sample 4, Figure 3). This shows that using the alkoxysilane derivative of the carborane dopant molecule and the SiO_2 of the source wafer as a backside capping layer effectively leads to (at least) the same level of doping as realized by MLD. The slightly lower R_s achieved by MLCD is attributed to the SiO_2 layer that is grown using thermal oxidation, which provides a higher quality oxide compared to sputtered SiO_2 that is generally used as a capping layer in MLD, and consequently lower losses of the dopant atoms are observed. This is in agreement with the observation by Javey and co-workers[5] that the Si:O stoichiometry of the silicon oxide capping layer has an effect on the diffusion efficiency.

Apparently, the source substrate is capable of performing multiple doping steps of different targets. This was demonstrated by the measurements of the sheet resistance of samples 2 and 3 in Figure 3. The gradual increase of R_s from samples 1 to 3 indicates the decreasing amounts of the dopants being incorporated into the targets. As mentioned above, the capability of performing multiple doping steps with the same source substrate shows that the dopant on the source substrate does not fully deplete during a single RTA step. Residuals of the remaining dopant molecules, deposited within the silicon oxide layer after the first annealing step, can still function as the dopant source in subsequent annealing steps. This offers the possibility to reuse the source substrate, or to use multiple annealing steps to tune the level of doping.

Secondary ion mass spectrometry (SIMS) was used to investigate the doping depth and boron profile in a target substrate that underwent the MLCD process (Figure 4). These

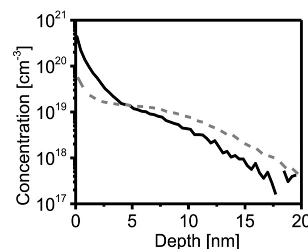

Figure 4. Boron dopant profiles measured by time-of-flight secondary ion mass spectrometry (TOF-SIMS) on a MLCD sample using a carboranyl-alkoxysilane (black solid line), and on a MLD-doped sample using a carborane alkene (gray line),[16] annealed under the same RTA conditions.

findings were compared to a profile obtained for a MLD-doped sample using a carborane alkene under the same RTA conditions and reported previously.[16] The MLCD approach resulted in a higher surface concentration compared to the MLD sample. The dopant extended to roughly the same depth in both cases, although the MLCD sample shows a steeper profile. The total area dose of the dopant for MLCD was 4.4×10^{13} cm^{-2}, while the one for MLD was 2.2×10^{13} cm^{-2}. This agrees well with the results from the R_s measurements, and confirms that the modified MLCD process is capable of reaching similar (or slightly higher) levels of doping as MLD. Given that MLCD requires incompatibility issues, this makes MLCD a promising alternative to MLD for the doping of silicon structures, in particular on SOI wafers where the use of fluoride etching must be avoided.

In the foregoing discussion it was indicated that the dopant was not fully depleted after the first annealing step. To quantitatively study the relation between the amount of dopant in the monolayer on the source substrate and the amount of the dopant that diffuses into the target during RTA, a carboranyl-alkoxysilane monolayer-covered source substrate was examined with SIMS to determine the amount of dopant per area. The measured areal dose was 2.3×10^{15} cm^{-2}. Comparing this areal dose to the one measured on the silicon target after annealing (sample 1), we note that the in-diffusion efficiency of the doping process is only about 2%. This low diffusion efficiency is attributed to the limited solid solubility of boron in silicon and the low thermal budget,[16,17] arising from the short annealing time used here during the RTA step.

CONCLUSIONS

An improved MLCD process was reported in this paper. A Si wafer with a thermally grown SiO_2 layer was used as the source substrate. A monolayer of an alkoxysilane-functionalized carborane was formed on this SiO_2 layer and used as the dopant source. This methodology provides two main advantages compared to the original MLCD process: (i) silane chemistry is more developed and employs less harsh reaction conditions than the monolayer formation on H-terminated

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silicon, and (ii) the use of silicon oxide provides a better capping function than silicon.

Upon annealing, R_s and SIMS measurements revealed similar dopant incorporation levels as obtained by MLD. We also found that the source substrate was capable of performing doping on multiple target substrates by repeating the annealing on other target substrates in series using the same source substrate. By quantifying the dopant areal doses on the source and target wafers, the dopant diffusion efficiency was found to be 2%. This offers potential for reusing the source substrate.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.7b00157.

Procedures for monolayer formation, rapid thermal annealing, analysis, and electrical measurements (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: j.huskens@utwente.nl.

ORCID

Rosario Núñez: 0000-0003-4582-5148

Jurriaan Huskens: 0000-0002-4596-9179

Notes

The authors declare no competing financial interest.

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