

Spin-On Organic Polymer Dopants for Silicon

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S Supporting Information

ABSTRACT: We introduce a new class of spin-on dopants composed of organic, dopant-containing polymers. These new dopants offer a hybrid between conventional inorganic spin-on dopants and a recently developed organic monolayer doping technique that affords unprecedented control and uniformity of doping profiles. We demonstrate the ability of polymer film doping to achieve both p-type and n-type silicon by using boronand phosphorus-containing polymer films. Different doping mechanisms are observed for boron and phosphorus doping, which could be related to the specific chemistries of the polymers. Thus, there is an opportunity to further control doping in the future by tuning the polymer chemistry.



SECTION: Energy Conversion and Storage; Energy and Charge Transport

The semiconductor industry demands silicon-doping techniques that produce precisely controlled doping profiles, a requirement that presents many technical challenges. Dopant atoms must be incorporated into the silicon lattice without disrupting the lattice or damaging the substrate. Furthermore, it is desired that the dopant concentration be precisely controlled and demonstrate uniformity over large areas.

One conventional doping method is ion implantation, which involves the bombardment of silicon with high-energy dopant ions that replace Si atoms in the lattice. Ion implantation results in excellent doping uniformity over large surface areas. However, the process also produces point defects and vacancies in the lattice, which interact with the dopants to broaden the junction profile, limiting the formation of sub-10 nm doping profiles.^{1–5} This depth limitation will become increasingly restrictive as semiconductor electronic devices are scaled to nanometer dimensions.^{1,2,6–10} Furthermore, ion implantation is incompatible with nonplanar, nanostructured materials because the energetic ions have significant probability of penetrating completely through the nanostructure without remaining in the lattice while causing significant crystal damage.¹¹

A second conventional method is to use spin-on dopants. This method entails spinning a dopant-containing solution onto silicon substrates, which is followed by a thermal annealing step during which the dopants diffuse into the substrate. Often times, a prediffusion annealing step is required to "glassify" the spin-on dopant layer. The dopant-containing solution usually contains either a mixture of SiO₂ and dopant or silicon-containing polymers with dopant atoms incorporated into the polymer (for example, phosphosilicates or borosili-

cates). Spin-on doping is a simple, low-cost, nondestructive technique, but it suffers from a lack of dose control and uniformity over large areas. Furthermore, spin-on dopants often leave behind undesirable residues. While pure SiO_2 and silicates are easily removed with wet etchants, the presence of residual organics from the solvent during the annealing process results in chemically modified layers that are very difficult to remove.¹²

Another approach currently under investigation for obtaining doped nanomaterials is the direct incorporation of dopants during nanomaterial synthesis.^{13–17} This approach has the advantage of producing high-quality doped lattices on the nanoscale but introduces many synthetic, scale-up, and integration challenges that still must be overcome.

Recently, a monolayer doping procedure has been developed that overcomes the difficulties of conventional technologies and achieves high-quality doping profiles with high areal uniformity.^{18,19} During this procedure, a covalently bound, self-assembled monolayer of dopant-containing organic molecules is formed on the surface of silicon substrates. In a subsequent thermal annealing step, the dopant atoms are diffused into the silicon lattice (see Figure 1a). Because of the inherent uniformity of the self-assembled monolayer, as well as the ability to tune the chemistry of the dopant-containing organic molecule, this approach affords unprecedented control and uniformity of doping profiles. Monolayer doping has also resulted in the demonstration of the shallowest junctions

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Figure 1. (a) Monolayer doping procedure, adapted from ref 18, and (b) spin-on organic polymer doping procedure.

reported to date¹⁹ and is a nondestructive technique, compatible with nonplanar, restricted-dimension nanostructured substrates.¹⁸

Here, we extend the use of organic dopant molecules in the monolayer doping technique to introduce a new class of spinon polymer dopants. In effect, these new spin-on dopants offer a hybrid between the monolayer doping technique and traditional inorganic spin-on dopants. As shown in Figure 1b, organic, dopant-containing polymer films are spun onto a silicon substrate from solution, and the dopant atoms subsequently diffuse into the silicon substrate during a rapid thermal annealing step. Like the organic monolayer dopants, the polymer chemistry is easily tuned to incorporate whichever dopant is desired. For example, in this work, we demonstrate the use of both boron- and phosphorus-containing polymers for obtaining p- and n-type doped silicon, respectively. In contrast to traditional inorganic spin-on dopants, the organic, dopantcontaining polymer films do not survive the annealing step. While the dopant atoms in the portion of the polymer film closest to the substrate diffuse into the silicon, the polymer film simultaneously burns away beginning at the film-air interface. We anticipate that this new doping mechanism may lead to easier film removal after the annealing step, compared to traditional inorganic spin-on dopants.

The chemical structures of the boron- and phosphoruscontaining polymers used in this study are shown in Figure 2. Polymer films were spin-coated from dilute solution in toluene or chloroform onto HF-treated, high-resistivity (>10⁴ Ω -cm, >1.8 × 10⁵ Ω/\Box) (100) silicon substrates (Silicon Valley Microelectronics; Santa Clara, CA). Concentrations ranging between 1 and 20 mg/mL and a spin speed of 2000 rpm were



Figure 2. Dopant-containing polymers used in this work.

used to obtain thicknesses varying between 6 and 120 nm, which were determined by ellipsometry. The substrates with polymer films underwent rapid thermal annealing under an argon gas purge using a Heatpulse 210T RTA system. The temperature was ramped from room temperature to either 950, 1000, or 1050 °C over the course of 20 s and then held at the annealing temperature for either 10, 30, or 60 s before cooling back to room temperature over the course of ~20 s.

Highly p- or n-type doped substrates are produced $(n^+/p^+$ n^{+2}/p^{+2}), as evidenced by four-point probe measurements and the resulting sheet resistances, R_S. For example, silicon substrates coated with a 17 nm thick film of the boroncontaining polymer and annealed at 1000 $^{\circ}$ C for 30 s have a R_{s} of 2.2 \times 10³ Ω/\Box . Within error, this is the same as the R_s of ptype doped substrates obtained using the monolayer doping procedure with the same annealing temperature and time. Silicon substrates coated with an 18 nm thick film of the phosphorus-containing polymer and annealed at 1000 °C for 30 s have a $R_{\rm S}$ of 5.4 \times 10² Ω/\Box , which is higher but on the same order of magnitude as that achieved by the monolayer ntype doping procedure.¹⁸ Note that the n-type doped substrates have lower sheet resistance for a given set of annealing conditions due to the higher solubility and diffusion coefficient of phosphorus in silicon compared to those of boron. $^{20-23}$

The resulting dopant profiles in silicon can be controlled by tuning the annealing conditions. As shown in Figure 3, the sheet resistances of n-type and p-type doped silicon substrates decrease with increasing annealing time and temperature. The decrease with temperature is due to the increased solubility and diffusion of the dopant in silicon at elevated temperatures, while the decrease with time is due to the longer time available for dopant molecules to diffuse into the silicon substrate.

Secondary ion mass spectrometry (SIMS) experiments that measured the depth profiles of the dopant atoms in the silicon substrate after doping confirm that the dopant atoms penetrate deeper into the silicon substrate for higher annealing temperatures and longer annealing times (Figure 4). The sharp decrease in dopant concentration near the surface followed by a more gradual decrease in dopant concentration at greater depths is known as the "kink-and-tail" feature and is commonly observed for conventional and monolayer doping procedures.^{24,25} The R_S can be estimated from the SIMS concentration profiles using the relationship



Figure 3. Sheet resistance, R_{s} , for p-type (boron) (a) and n-type (phosphorus) (b) doped silicon substrates as a function of annealing time and temperature. Boron-containing films were 17 nm thick before annealing, and phosphorus-containing films were 18 nm thick.



Figure 4. Depth profiles of phosphorus dopant atoms in silicon substrates as a function of annealing temperature, using a fixed annealing time of 30 s (a), and as a function of annealing time, using a fixed annealing temperature of 1000 $^{\circ}$ C (b). The thickness of the polymer films before annealing was 16 nm. The control experiment was performed using a silicon substrate without a polymer film that underwent the rapid thermal annealing procedure.

$$\frac{1}{R_{\rm S}} = \int_0^l q N(x) \mu(x) \,\mathrm{d}x \tag{1}$$

where *l* is the depth of the doped region of the substrate, *q* is the charge, N(x) is the dopant concentration from SIMS as a function of depth in atoms/cm³, and $\mu(x)$ is the carrier mobility as a function of depth in cm²/(V s) and is estimated by^{18,26}

$$\mu(x) = 68.5 + \frac{1345.5}{1 + \left(\frac{N(x)}{9.2 \times 10^{16}}\right)^{0.711}}$$
(2)

The values of R_S estimated from the SIMS dopant concentration profiles are in reasonable agreement with those obtained from four-point probe sheet resistance measurements. For example, the R_S estimated from SIMS profiles for silicon substrates coated with 16 nm phosphorus-containing films and annealed at 1000 °C for 30 s is 518 Ohm/ \Box , compared to 540 Ohm/ \Box obtained from four-point probe measurements.

The dopant penetration depths observed in the SIMS profiles are also reasonable based on the known diffusion coefficients for phosphorus and boron atoms in silicon. For example, the estimated diffusion lengths for the phosphorus-doped substrates depicted in Figure 4b are estimated as $2(Dt)^{1/2}$ to be 10, 18, and 25 nm for annealing times of 10, 30, and 60 s, respectively, in reasonable agreement with the observed depth profiles from SIMS.

Interestingly, in the case of phosphorus-doped substrates, the concentration of phosphorus at the surface actually decreases slightly for higher annealing temperatures and longer annealing times (Figure 4). This indicates that a "limited source" diffusion model is appropriate for describing phosphorus doping. In other words, during the rapid thermal annealing step, the polymer film does not supply sufficient phosphorus atoms to maintain the concentration of phosphorus just under the surface of the silicon substrate at the equilibrium phosphorus solubility. The surface concentrations measured in this work at 1000 °C range from 3×10^{20} to 8×10^{20} atoms/cm³ depending on the annealing time, whereas the equilibrium solubility of phosphorus in silicon at 1000 °C has been previously measured to be 1×10^{21} atoms/cm^{3,21} In further support of a limited source diffusion model, the total phosphorus contents in the silicon substrates after annealing for 10, 30, and 60 s, determined by integrating the SIMS profiles in Figure 4b, are similar $(1.4-1.5 \times 10^{14} \text{ atoms/cm}^2)$.

Recall that the polymer film burns away during the annealing step. Therefore, there is a race between dopant atoms diffusing down into the silicon substrate and the film burning away starting from the top of the film. In order to try to increase the amount of phosphorus doping, we increased the phosphorus film thickness. This was expected to both increase the overall phosphorus "source" concentration as well as increase the amount of time for the polymer film to burn, giving the dopant atoms more time to diffuse into the silicon substrate. As shown in Figure 5, the amount of phosphorus incorporated into the silicon substrate indeed increases with increasing film thickness,



Figure 5. Depth profiles of phosphorus atoms in doped silicon substrates (a) and sheet resistances of boron- and phosphorus-doped silicon substrates (b) using polymer films of varying thickness. All substrates were annealed at 1000 $^{\circ}$ C for 30 s.

and there is a corresponding decrease in the measured $R_{\rm S}$. However, increasing the film thickness only helps to a point. The $R_{\rm S}$ seems to level off at about $3 \times 10^2 \ \Omega/\Box$ for film thicknesses between about 40 and 90 nm, under which conditions the surface phosphorus concentration is still lower than the equilibrium solubility (and the $R_{\rm S}$ is still about twice as high as that obtained using the monolayer doping procedure¹⁸). Interestingly, for the two thickest films measured by SIMS (56 and 100 nm), phosphorus-containing residue on the order of 10 nm thick remained on the surface of the substrate after annealing, as identified by phosphorus SIMS measurements (Figure S2 in the Supporting Information).

Unlike phosphorus doping, boron doping is not dependent on the polymer film thickness (Figure 5b). Therefore, for the annealing temperatures and times probed in this study, boron doping can be described by a "constant source" diffusion model, meaning that even for the thinnest films, the polymer film supplies sufficient dopant atoms such that the concentration of boron atoms just under the surface of the silicon substrate is equal to the maximum solubility of boron in silicon. The dopant profile then depends only on the annealing time and temperature. As shown in Figure 6, the concentration of boron right at the surface of doped silicon substrates is constant for various annealing times and is close to the equilibrium solubility of 2×10^{20} to 4×10^{20} atoms/cm³,^{20,22,23} while the concentration of boron deeper into the silicon substrate increases for longer annealing times. Furthermore, the total boron content increases from 3.0 \times $10^{13}~atoms/cm^2$ for an annealing time of 10 s to 3.9×10^{13} atoms/cm² for an annealing time of 60 s (determined by integrating the SIMS profiles in Figure 6).

The reasons for the differences between boron and phosphorus doping are somewhat unclear. The doping



Figure 6. Depth profiles of boron atoms in doped silicon substrates annealed at 1000 °C for various annealing times. The thickness of the polymer films before annealing was 20 nm. The control experiment was performed using a silicon substrate without a polymer film that underwent the rapid thermal annealing procedure.

efficiency for phosphorus atoms using the monolayer procedure is 95%, which is much greater than that for boron (33%).¹⁸ Thus, the limited source diffusion for phosphorus cannot be explained by a decreased inherent penetration efficiency. It also cannot be explained by a decreased dopant concentration in the film because the concentration of phosphorus in the phosphorus-containing polymer is greater than that of boron in the boron-containing polymer. We anticipate that the difference has to do with the race between dopant diffusion and film degradation that occurs during annealing. It is possible that the boron-containing polymer films burn more slowly. Thermal gravimetric analysis (TGA) shows that both types of polymer films burn at similar temperatures (Figure S3 in the Supporting Information), but the time scale for TGA is much slower than that for rapid thermal annealing (5 °C/min versus >300 °C/ sec). The surface properties of the boron films could also be altered during the burning process in such a way that promotes the diffusion of dopant atoms down into the silicon substrate compared to the phosphorus case. For example, dopant diffusion into silicon is more likely if solubility in the top portion of the film is low. Another possible explanation for limited source diffusion of phosphorus is that phosphorus has a greater solubility in silicon than does boron, and the polymer film cannot supply the greater amount of dopant atoms (despite the greater dopant content in the phosphoruscontaining polymer compared to that in the boron-containing polymer). In the future, we will use polymer films with a higher phosphorus content to try to improve phosphorus doping, and we will investigate the role of polymer chemistry in promoting doping during the dopant diffusion/film burning step. Detailed postannealing surface analysis will also be necessary to determine how cleanly the polymer films burn away for different polymer chemistries, film thicknesses, and annealing conditions.

One danger when using carbon-containing polymer films for doping is the unintended incorporation of carbon into the silicon substrate. Junction leakage currents of substrates doped using the monolayer doping procedure suggested that carbon incorporation is not a concern using that technique,¹⁹ but significantly more carbon is present during the polymer thin film procedure. We performed carbon SIMS experiments to show that there was negligible carbon incorporated into the doped substrates. We found that the carbon contents of boronand phosphorus-doped substrates were not significantly different from that of a control substrate, which went through the rapid thermal annealing procedure but did not have a polymer film deposited on it beforehand (Figure S4 in the Supporting Information).

In summary, we have introduced a new class of spin-on dopants composed of organic, dopant-containing polymers. These dopants afford excellent n-type and p-type doping and offer a hybrid between conventional spin-on inorganic dopants and the recently developed organic monolayer doping technique. In contrast to traditional inorganic spin-on dopants, the organic polymer films burn away during the annealing step. We anticipate that this new mechanism may lead to easier film removal after annealing. Detailed postannealing surface analysis is underway to determine how cleanly the polymer films burn away for different polymer chemistries, film thicknesses, and annealing conditions.

The p-type doping of silicon achieved in this work using boron-containing polymer films of PVBAPE follows a "constant source" diffusion mechanism, where the concentration of boron at the surface of the silicon substrate is equal to the equilibrium boron solubility, and the depth profile is determined by the annealing time and temperature. On the other hand, the n-type doping of silicon achieved in this work using phosphoruscontaining polymer films of PDEVP follows a "limited source" diffusion mechanism, where the concentration of phosphorus at the surface is less than the equilibrium phosphorus solubility, and the amount of phosphorus doping increases with increasing polymer film thickness. On the basis of these differences, we believe that there is further opportunity to tune the doping mechanism by tuning the polymer chemistry. Future work will aim to improve doping, for example, by using polymers with a higher concentration of dopant molecules and by learning more about the mechanism by which the polymer chemistry promotes doping during the dopant diffusion/polymer film burning step.

ASSOCIATED CONTENT

Supporting Information

Details of dopant-containing polymer syntheses, SIMS experimental details, phosphorus SIMS profiles for substrates doped with thick films, TGA of boron- and phosphorus-containing polymers, and carbon depth profiles from SIMS. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Supporting Information for:

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Dopant-Containing Polymer Synthesis

The boron-containing polymer, poly(vinylboronic acid pinacol ester) (PVBAPE), was synthesized according to a previously reported method.¹ In brief, vinylboronic acid (2.5g) was converted to the pinacol ester by stirring with a slight molar excess of pinacol (2.1g) in dichloromethane (50mL) for 24 hrs at room temperature over molecular sieves (1.0g). The esterified monomer (1.0g) was polymerized for 16 hours at 70 °C by reversible addition-fragmentation chain transfer polymerization, using 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid as the chain transfer agent (0.0155g), azobisisobutyronitrile (AIBN) as the initiator (0.0011g), and anhydrous anisole as the solvent (1mL). The resulting polymer was isolated by precipitation into cold (-20 °C) hexanes. The number-averaged molecular weight, M_N , and dispersity were found to be 10 kg/mol and 1.28, respectively, using gel permeation chromatography (GPC) with polystyrene molecular weight standards. Initially, a series of polymers with a range of molecular weights were synthesized. However, the molecular weight proved to not affect the doping results, so the polymer with M_N =10 kg/mol was used for the entirety of the work reported here.

The phosphorus-containing polymer, poly(diethyl vinylphosphonate) (PDEVP) was synthesized via anionic polymerization of diethyl vinylphosphonate (DEVP). DEVP (6.0mL) and diphenylethylene (DPE, 0.5mL) were degassed using three freeze-pump-thaw cycles, dried by stirring overnight over molecular sieves or calcium hydride, respectively, and distilled into flame-dried ampules. Anhydrous tetrahydrofuran (THF, 125mL) was degassed and cleaned with sec-butyl lithium (300 μ L) at -78 °C for 30 min (and was then warmed to room temperature overnight). DPE was cannula-transferred into the THF at -78 °C, and then initiated with sec-butyl lithium (150 μ L of 1.4 M solution in cyclohexane). After 30 min, DEVP was transferred to the reaction vessel and the polymerization was allowed to proceed for 3 hours before termination with methanol. The resulting polymer was precipitated into cold (0 °C) hexanes. The theoretical molecular weight was calculated to be 31 kg/mol based on the amount of monomer and initiator used. However, the actual molecular weight could not be determined by GPC due to the polymer sticking on the columns.

All materials were purchased from Sigma Aldrich (St. Louis, MO). AIBN was recrystallized from methanol, anhydrous THF was dried by passing through an alumina column, and all other materials were used as received or purified as described above.

Secondary-Ion Mass Spectrometry (SIMS) Measurements

SIMS profiles were measured by Charles Evans Analytical Group (Sunnyvale, CA). The surface of the substrate was determined by monitoring the secondary ion intensity for Si, which sharply increases at the surface of the silicon substrate, and then remains constant. The surface of the substrate was taken to be the point at which the secondary ion intensity for Si reached 75% of the plateau value. For example, see Figure S1.



Figure S1. Phosphorus and silicon SIMS profiles doped silicon substrates annealed at 1000 °C for 30 sec, using a 16 nm phosphorus-containing polymer film. The substrate surface was designated the depth at which the silicon signal reached 75% of it's plateau value. The phosphorus signal at shallower depths is likely attributed to residual organic material on top of the substrate.

Phosphorus SIMS of Substrates Doped with Thick Films



Figure S2. Depth profiles of phosphorus atoms in silicon substrates doped using the two thickest phosphorus-containing polymer films, 56 nm and 100 nm, using a 30 sec anneal at 1000 °C. The SIMS profiles suggest that there is phosphorus-containing residue on the order of 10 nm thick that remains on the surface of the substrate after annealing.

Thermal Gravitational Analysis (TGA)



Figure S3. TGA results for the boron-containing polymer (a) and the phosphorus-containing polymer (b). The temperature was increased at a rate of 5 °C/min. Both polymers burn at similar temperatures. The two-step burning method is attributed to the preliminary degradation of the side chains and secondary degradation of the main chain of the polymers.

Carbon SIMS Profiles



Figure S4. Depth profiles of carbon atoms in doped silicon substrates annealed at 1000 °C for 30 sec, using boron- and phosphorus-containing polymer films of various thicknesses. The control experiment was performed using a silicon substrate without a polymer film that underwent the rapid thermal annealing procedure. The carbon contents in the doped substrates are not significantly different from the control.

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