



Review article

Doping of semiconductors by molecular monolayers: monolayer formation, dopant diffusion and applications

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ABSTRACT

The continuous miniaturization in the semiconductor industry brings electronic devices with higher performance at lower cost. The doping of semiconductor materials plays a crucial role in tuning the electrical properties of the materials. Ion implantation is currently widely used. Yet, this technique faces challenges meeting the requirements for smaller devices. Monolayer doping (MLD) has been proposed as one of the alternative techniques for doping semiconductors. It utilizes dopant-containing organic molecules and grafts them onto semiconductor surfaces. The dopant atoms are subsequently driven into the substrate by high temperature annealing. MLD has shown the capability for ultra-shallow doping and the doping of 3-D structures without causing crystal damage. These features make this technique a promising candidate to dope future electronic devices. In this review the processes for monolayer formation and dopant incorporation by annealing will be discussed, as well as the applications of MLD in device fabrication.

1. Introduction

The advancement in the semiconductor industry relies on the downscaling of devices towards nanometer dimensions for better performance and lower costs. The semiconductor industry has been putting resources into research and development (R & D) to push the technology towards miniaturization at the pace set by Moore's Law. In recent years, as the dimensions of transistors have reached the sub-30 nm scale, technology challenges have arisen that make it increasingly difficult for the industry to keep up with this pace. For instance, according to the 2013 International Technology Roadmap for Semiconductors (ITRS), for achieving a 7 nm node, predicted to be reached in 2017, the junction depth X_j needs to be 6.1 nm, which is difficult to realize in 2D structures [1]. In recent years, to circumvent such fabrication difficulties and also to achieve better device performance, the traditional 2-D planar device architecture is being changed into 3-D finFET structures. When focusing on the doping process, the currently employed beamline implantation, which is routinely used for finFET fabrication, is also facing challenges from the crystal damage caused by incident ions and by shadowing effects arising from the directional nature of the beamline implantation.

Monolayer doping (MLD) has been proposed by Javey et al. as an

alternative doping technique (Fig. 1) [2,3]. This technique utilizes dopant-containing molecules, which are covalently bound to the silicon surface. After applying a capping layer to prevent premature loss of the dopant molecules upon heating, this is followed by an annealing process to decompose the molecules and drive the dopants into the silicon substrate. After removal of the capping layer, a thin doped layer or junction is then achieved. The self-limiting nature of the molecular monolayer provides a well-defined dopant dose. MLD has the capability of forming shallow doped layers of less than 10 nm with sharp boundaries. Moreover, the technique avoids the crystal damage occurring during ion implantation and is capable of doping 3-D structures without shadowing effects by the conformal nature of the monolayer formation process.

This review aims at providing a comprehensive overview of the MLD technique from grafting of the dopant adsorbate onto the silicon surface to the incorporation of the dopant via annealing including strategies to control the depth and the level of doping. Finally, applications of MLD are discussed.

2. Grafting of the monolayer

MLD primarily relies on hydrosilylation to covalently bind the dopant-containing adsorbate onto a non-oxidized silicon surface.

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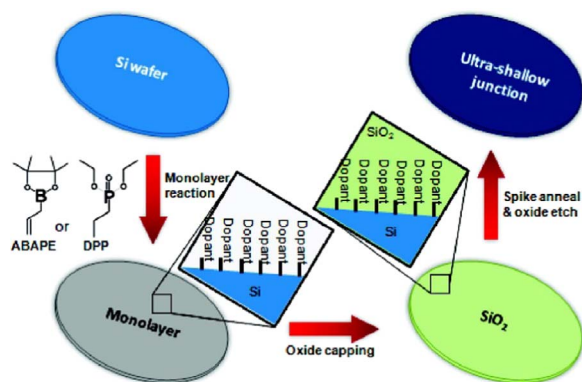


Fig. 1. Schematic representation of the monolayer doping (MLD) process. Figure adopted from Ref [3]. © 2009 American Chemical Society.

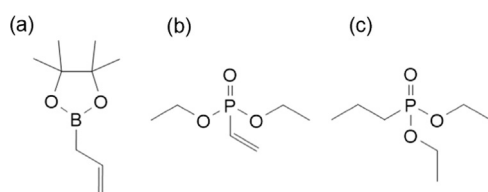


Fig. 2. Structures of the commonly used dopant adsorbate for MLD: (a) allylboronic acid pinacol ester (ABAPE); (b) diethyl vinylphosphonate (DVP); and (c) diethyl 1-propylphosphonate (DPP).

Terminal alkene ($C=C$) or alkyne ($C\equiv C$) molecules are used to bind to a hydrogen-terminated silicon surface. For MLD, the adsorbate needs to contain a dopant atom. For example, allylboronic acid pinacol ester (ABAPE, Fig. 2a) is commonly used as a boron source [2]. For phosphorus doping, diethyl vinylphosphonate (DVP, Fig. 2b) has been reported but also diethyl 1-propylphosphonate (DPP, Fig. 2c), which lacks an alkene moiety, has been demonstrated to function as a phosphorus source. The bonding mechanism of DPP onto the silicon surface is not quite understood, but based on reports by Javey and others it seems to form a densely packed monolayer on silicon like the other dopant adsorbates. [2,4–6].

2.1. Hydrosilylation

The hydrosilylation process is preceded by cleaning the silicon surface and removing the native oxide in an aqueous solution of HF or NH_4F . This creates a hydrogen-terminated surface. The silicon substrate is then submerged in the liquid alkene or a solution thereof, and the hydrosilylation reaction is initiated by heating to 150–200 °C or by irradiation with light. The hydrosilylation on silicon was first reported

by Chidsey and coworkers in 1993 using the thermal method [7]. Later studies showed that UV light [8,9] and even white light [10,11] can be used to promote the reaction. The mechanism of the surface reaction was extensively studied by the groups of Chidsey and Zuilhof. It is generally believed that the hydrosilylation proceeds by a radical-chain mechanism [12], as shown in Fig. 3. Route 1 in Fig. 3 describes the widely accepted pathway under UV light, and route 2 describes the mechanism under thermal conditions or visible light at room temperature for the formation of the C-Si bond at the H-Si surface. By either route, the reaction provides a new silyl radical that can react further with another alkene. The reaction propagates until a densely packed monolayer is formed. An STM observation of the formation process by Eves et al. [13] showed island formation and chain propagation under mild light irradiation conditions.

Contact angle (CA), infrared spectroscopy, ellipsometry and X-ray photoelectron spectroscopy (XPS) are widely used to characterize the formed monolayers. CA goniometry is a quick and easy way to assess the packing quality of the monolayer. The measured CA depends on the wettability of the head group of the adsorbate molecules used. For molecules with a terminal methyl group this is normally between 107° and 110°. Infrared spectroscopy aims to measure the signal of the methylene group, e.g. its C-H vibrations, to confirm the presence of the organic monolayer on surface. Ellipsometry is used to measure the monolayer thickness, which depends on the length of the molecules used. The relation between the thickness of the monolayer and the density and size of the molecules has been extensively studied by the Zuilhof group [14,15]. XPS has been used to measure surface concentrations of carbon or other elements present in the adsorbate to determine the composition and the quality of the monolayer. Concretely, Wallart et al. developed a method which uses the XPS data to determine the surface packing density of the monolayer, by using the XPS signal intensity of carbon and silicon and attenuation of the Si substrate signal resulting from the coverage with a monolayer [16].

Monitoring the packing density is important for the function of the monolayer, for example, a densely packed monolayer provides a better shielding effect of the underlying Si surface to oxidation [12]. For MLD, its importance lies in knowing the initial amount of dopants present on the surface. The packing density of the monolayer formed by hydrosilylation of an alkene adsorbate to the H-terminated silicon surface can be understood as the percentage of the H-Si sites that are bonded to adsorbate molecules. A theoretical study has revealed that, due to the difference between the molecular size of an alkyl chain and the density of Si-H sites, a packing density of 69% represents the upper limit [17]. In practice, most reported packing densities for alkene molecules are around 50% [15,16,18]. In their initial work, Javey et al. estimated the maximum packing density for ABAPE and DPP using the footprint of the molecules and found them to be 4.9×10^{14} and $8.3 \times 10^{14} \text{ cm}^{-2}$, respectively [2]. This thus represents the maximum

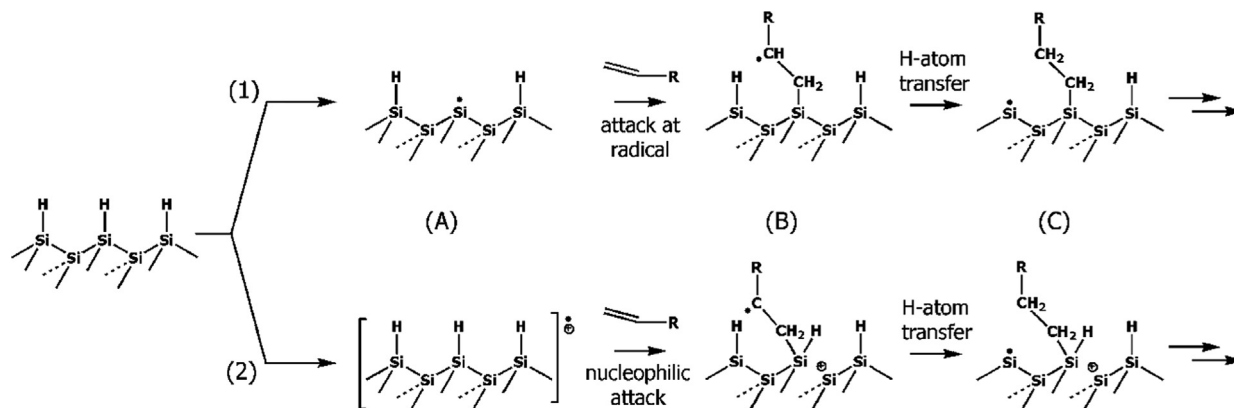


Fig. 3. The radical chain mechanism of alkenes initiated by (1) a radical initiator or UV light, or (2) thermal conditions or visible light irradiation. Figure adopted from Ref [12]. © 2010 American Chemical Society.

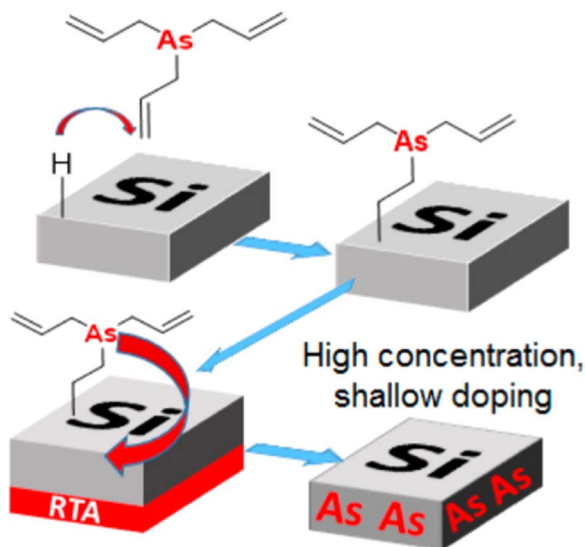


Fig. 4. Schematic representation of arsenic doping by MLD using triallylarsine [22]. © 2015 American Chemical Society.

areal dose for monolayer doping using these two molecules. A recent study [19] carried out by Arduca et al. using TOF-SIMS found the maximum packing density of DPP to be about $8 \times 10^{14} \text{ cm}^{-2}$, very close to the one predicted by Javey et al. A higher doping dose using MLD can thus be realized in two ways: either using a different molecule that has more than one dopant atom in its structure or using multiple MLD steps on a single substrate. These are discussed in Sections 2.3 and 3.4, respectively.

Early studies on hydrosilylation were reported using the neat alkene compound. Later on, Sieval et al. [20] systematically studied the hydrosilylation using diluted adsorbate in various of solvent. They reported that using mesitylene as solvent, a densely packed monolayer can be formed using an alkene concentration as low as 2.5%. Comparing their reaction conditions with previously reported ones using the neat compound [14,21] shows that no substantial increase in reaction time or temperature is needed. This reduces considerably the amount of alkene required for the hydrosilylation, and thus opens the scope to the use of more complex, functional molecules to be used as adsorbates. MLD can benefit from using such diluted compounds, as the dopant adsorbate is usually costly and a large volume is needed to immerse the wafer and to thus achieve full-wafer scale doping.

Most MLD processes use boron- or phosphorus-containing compounds as the dopant adsorbate to achieve p- and n-type doping, respectively. Recently, the doping of arsenic was reported using triallylarsine (TAA) as the dopant adsorbate (Fig. 4) [22]. Arsenic is an n-type dopant that has a lower diffusivity and higher solubility than phosphorus. Using As would potentially help achieve shallower junctions with a higher surface dopant concentration.

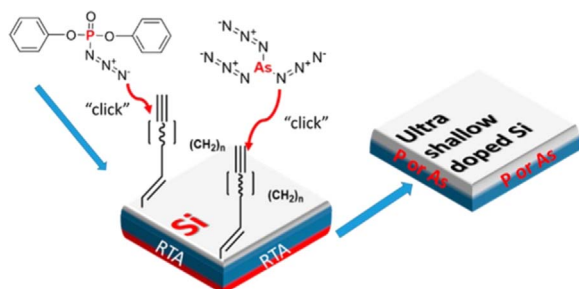


Fig. 5. Schematic representation of the two-step surface functionalization process to graft a dopant adsorbate onto silicon surface leading to surface doping [24]. © 2016 American Chemical Society.

Besides alkene molecules, also alkynes can undergo the hydrosilylation reaction with a H-terminated silicon surface [23]. Compared to alkenes, alkynes can form monolayers with higher packing densities, and the monolayer formation can be performed under milder conditions [12,15]. Connell et al. recently reported the use of a dialkyne to graft a dopant-containing azide by a two-step functionalization process [24]. As shown in Fig. 5, the silicon surface was first functionalized with the dialkyne through hydrosilylation. Thereafter, the P or As-containing azide was bound to the terminal alkyne by the copper-catalyzed alkyne-azide cycloaddition (CuAAC) reaction.

2.2. MLD on other substrates

A reaction similar to hydrosilylation can also be applied to H-terminated germanium surfaces. This reaction is known as hydrogermylation [25–27]. Functionalized alkene and alkyne molecules can be grafted onto the Ge surface by this route. The formation of such monolayers and MLD on Ge substrates is less studied than on Si surfaces, which follows the general trend of a much stronger development of Si technology compared to Ge. Yet, Ge is an increasingly studied substitute material for silicon due to its high carrier mobility. Long et al. reported MLD on germanium using hydrogermylation using triallylarsine as the dopant adsorbate [28]. A dopant concentration of $6.0 \times 10^{18} \text{ cm}^{-3}$ was achieved.

The concept of forming a dopant-containing monolayer to immobilize the dopants on the substrate, and then driving the dopant into the substrate can also be extended to III-V semiconductors. The doping of InAs [29], InP [30], GaAs [31], and InGaAs [32–34] has been reported using the MLD concept. In these studies, either sulfur or silicon was used as the dopant. Ammonium sulfide ($(\text{NH}_4)_2\text{S}_x$) [35,36] and a disilane or silane [33] were used as the sulfur and silicon-containing adsorbates, respectively. Also ultra-shallow doping could be achieved by MLD in these materials [37,38].

2.3. Localized doping and dose control

Monolayer formation can be combined with a patterning technique to create a patterned monolayer, and thus achieve localized doping. Most of the MLD studies described above utilize a homogeneously covered monolayer to achieve homogeneous doping of the entire silicon surface. In contrast, patterning of the monolayer has been achieved by UV light irradiation through a mask to initiate the light-driven hydrosilylation reaction with spatial control [8,39]. Alternatively, the hydrosilylation process can be followed by a lithography step and spatioselective etching of the organic monolayer [40]. Using this method, Voorthuijzen et al. have reported the localized doping by combining monolayer formation with nanoimprint lithography, as shown in Fig. 6 [41].

The semiconductor industry relies on varying the dopant concentration to the desired level. Tuning of the doping concentration in MLD has been limited to the process parameters of the thermal annealing step. Recently, however, we reported that tuning of the doping level can

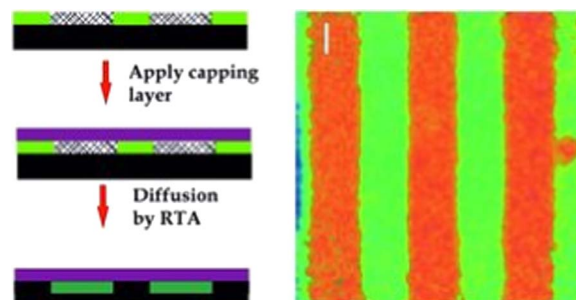


Fig. 6. (left) Schematic representation of the spatioselective functionalization of a silicon surface and the localized doping achieved. (right) The resulting localized doping observed by SIMS [41]. © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

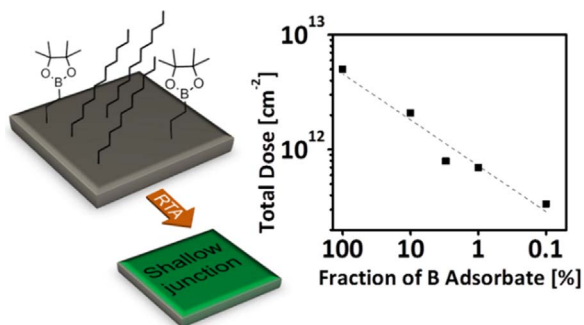


Fig. 7. Schematic representation of the mixed monolayer doping concept [42]. The dopant adsorbate (ABAPe in the figure) is mixed with an alkene (1-undecene) that lacks dopant atoms. © 2015 American Chemical Society.

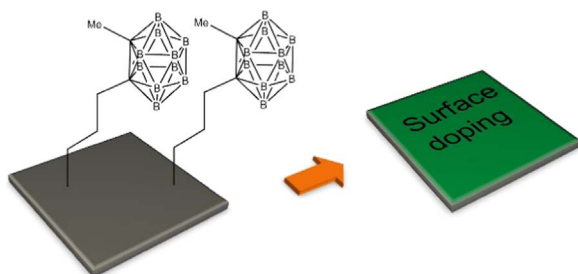


Fig. 8. Schematic representation of the use of carborane clusters to boost the boron doping level in silicon [43]. © American Chemical Society.

be achieved by mixing the dopant adsorbate with an alkene that lacks the dopant atoms [42], as shown in Fig. 7. Variation of the areal dose of more than one order of magnitude was reported by changing the fraction of the dopant adsorbate between 100% and 0.1%. Variation of the dopant dose of both boron and phosphorus was achieved effectively in this manner. This concept provides a new pathway to control the doping level using MLD, in particular when changing the annealing parameters is restrained by materials or process limitations.

Achieving a higher doping level by MLD is less straightforward. As discussed above, the maximum doping dose for MLD is limited by the packing density of the adsorbate molecules on the silicon surface. Thereby the only logical way to increase the doping dose beyond this level is to use adsorbates with multiple dopant atoms. Recently, we reported the doping of silicon by using boron-rich carborane clusters with ten boron atoms in their structure (Fig. 8) [43]. The 10 times increase in dopant atoms in the adsorbate resulted in an approximately 10 times increase of the doping level compared to the single-boron containing ABAPe under the same annealing conditions. This concept makes it possible to achieve a higher doping level in a one-step monolayer grafting and annealing process, which minimizes the thermal budget that the sample has to undergo.

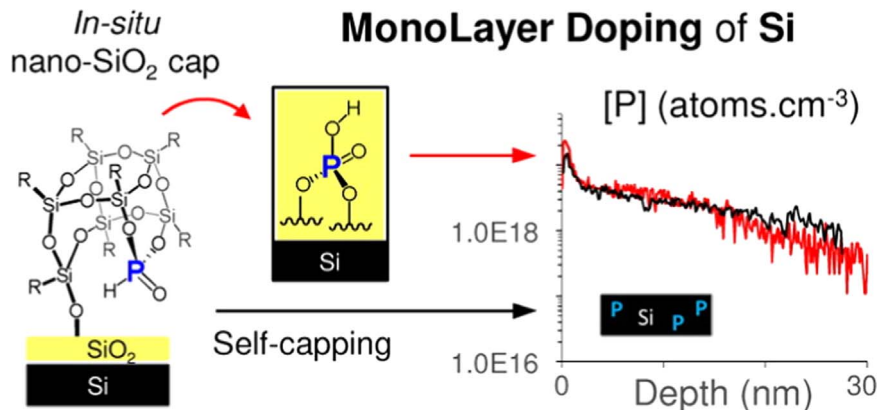


Fig. 9. Schematic representation of MLD with self-capping capability [51]. © 2016 American Chemical Society.

3. Diffusion of the dopants

In the typical MLD process, a capping layer of SiO₂ is deposited after grafting of the monolayer, and then the substrate is subjected to a thermal annealing process to decompose the dopant adsorbate molecules and drive the dopant atoms into the silicon substrate, forming a thin doped surface layer. The annealing temperature and time depend on the desired junction depth and on the diffusion characteristics of the dopant species.

3.1. Diffusion of the dopants

As a diffusion-based doping technique, MLD relies on a thermal process to drive the dopant into the silicon substrate. In the case of ultra-shallow doping, a higher solid solubility and a lower diffusivity are desired. Yet, both solubility and diffusivity are temperature dependent and increase with temperature. Annealing at a higher temperature is needed if a high doping concentration is desired. Meanwhile, to achieve shallow doping a short annealing step is required to avoid the dopant being driven deep into the substrate. Rapid thermal annealing or spike annealing with a temperature ramping rate above 50 °C/s is commonly used in the reported ultra-shallow doping processes using MLD [3]. A more rapid annealing process (such as laser annealing and flashlamp annealing) can achieve an even higher temperature ramping rate. However due to the presence of a capping layer in MLD (discussed below) and the fact that these annealing techniques melt and re-crystallize the materials, the applicability of these techniques for MLD seems to be less favorable.

Fick's law of diffusion is usually used to evaluate the diffusion processes in MLD. To predict the dopant profile, the boundary conditions must be known. The two most commonly used conditions are constant dose and constant concentration. At a constant dose, a limited, fixed amount of dopant is assumed to be incorporated into silicon during the annealing step, while constant concentration assumes a fixed surface concentration of the dopant that does not change during annealing. It might seem plausible that a constant dose is the primary mechanism in MLD as the amount of dopant is strictly limited by the monolayer. However, it was found that assuming a constant concentration is more applicable for spike annealing that aims to achieve shallow junctions [3]. The reported [3] areal dose indicated that only about 1% of boron of the initially bonded monolayer is actually incorporated into the silicon substrate during the annealing process.

3.2. Carbon contamination

Carbon contaminations diffused into the substrate during annealing is an issue faced by MLD. MLD relies on an organic compound that forms a Si-C bond to bind the dopant onto the silicon surface. Hence,

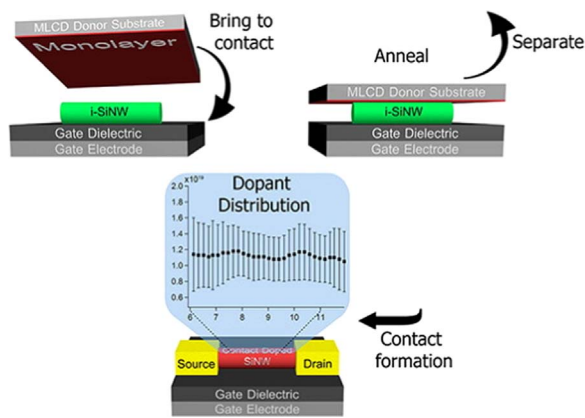


Fig. 10. Schematic representation of the monolayer contact doping (MLCD) process applied to silicon nanowires. © 2012 American Chemical Society.

carbon is inevitably introduced into the substrate together with the dopant during annealing. Carbon contamination in silicon has been well studied as it is also generally found in silicon wafers introduced during the wafer production process [44,45]. Javey et al. measured the leakage current of a device fabricated using MLD and reported no observable impact of the carbon incorporation despite its presence [3]. In fact, carbon is sometimes used as a co-implant in ion implantation to help achieving shallow junctions [46–48].

3.3. Capping layer

Capping layer deposition is necessary in MLD to avoid the escape of dopant atoms into the surroundings during thermal annealing. In their pioneering work [2], Javey et al. reported a substantial loss of boron atoms in the absence of a capping layer. Following this early work, SiO₂ is almost exclusively used as the capping layer in MLD. However, different deposition techniques of the SiO₂ capping layer have been reported, including evaporation [2,3,41], sputtering [42,43], and spin-coating of spin-on glass [49,50]. The SiO₂ deposited under vacuum (evaporation and sputtering) is expected to be oxygen deficient. It was noted by Javey et al. that the stoichiometry of the capping layer affects the dopant incorporation process [2], as the oxygen deficiency in the capping layer lowered the dopant incorporation in the substrate.

Recently, a self-capping MLD process (Fig. 9) [51] was reported by Alphazan et al. A hepta-isobutyl-polyhedral oligomeric silsesquioxane triester of phosphorus was used as the precursor to adhere the phosphorus dopant onto the silicon surface. The self-capping property arises from the silica-like silsesquioxane capping cage of the precursor. This obviates an additional capping layer deposition step.

3.4. Monolayer contact doping (MLCD)

The MLD process requires wet chemistry to covalently bind the monolayer onto the silicon surface. The process involves the removal of the native oxide layer in a fluoride-based etchant and immersion in organic solvent at elevated temperature. These steps pose a limitation for substrates with materials that are incompatible with such process steps. Yerushalmi and co-workers proposed monolayer contact doping (MLCD) to address this challenge (Fig. 10) [52,53]. The process involves the grafting of the dopant adsorbate onto a separate silicon substrate (the source wafer) different from the one that needs to be doped (the target wafer). The source wafer is then brought into contact with the target wafer and annealed in a furnace. The annealing process drives the dopant from the source wafer into both the source and target wafers. After cooling down and separation of the wafers a thin, doped surface layer is present on the target wafer. MLCD was demonstrated to dope silicon nanowires (Si NWs) on a silicon oxide layer, which is difficult to dope with regular MLD because the etching of the native

oxide on the Si NW would etch away the oxide as well. Moreover, MLCD can be repeated on a single target wafer to achieve higher doping levels [53]. A parallel p-n junction across nanowires was achieved using the MLCD concept with the nanowire sandwiched between two source wafers with boron and phosphorus dopant adsorbates followed by annealing [54].

4. Towards applications

4.1. MLD for electronic devices

The downscaling trend in the semiconductor industry is pushing technology towards smaller dimensions for higher performance and lower costs. As an example, in recent years, the channel thickness of the 3-D finFET is scaled down to sub-10 nm. Homogeneous doping of the, similarly sized, source and drain regions surrounding the gate of the 3D structure at such small dimensions becomes challenging for traditional doping techniques [55,56]. As shown by Duffy et al., the doping of such 3-D structures using ion implantation induces crystal damage that cannot be repaired by thermal annealing [57,58], because of the high surface to volume ratio of finFET structures. Consequently, alternative doping strategies are being intensively evaluated in recent years [59]. The potential of MLD in shallow doping and in doping nonplanar structures without causing crystal damage makes it one of the promising alternatives.

Ultra-shallow doping using MLD has been demonstrated shortly after its first reports [3]. Following those studies, MLD has been recognized by semiconductor industry as one of the potential doping strategies to manufacture next-generation CMOS or finFET devices [60,61]. Ang et al. explored the capability of MLD in the doping of finFET devices [62]. A damage-free doping of a finFET structure was achieved, while control samples doped by ion implantation showed crystal damage within the structure. MLD was also utilized to achieve a conformal shell doping on the finFET structures [63,64]. A better gate control appeared to result from the close proximity of the dopant to the gate. The doping of polycrystalline Si finFETs was reported using MLD [65], and junctions of sub-5 nm with a resistance in the range of kΩ were achieved.

Being a diffusion-based doping technique, some drawbacks of the diffusion process also apply to MLD. The upper concentration limit of the dopant is defined by the solid solubility of the dopant in the substrate. Secondly, independent control of the dopant concentration and the junction depth is challenging as both the solid solubility and diffusivity are temperature dependent. Thus, a higher dopant concentration comes with a higher thermal budget, which is sometimes not desired. These limitations can potentially hinder the application of MLD for certain applications.

4.2. MLD for solar cells

The increasing awareness of climate change calls for switching from traditional fossil fuels to cleaner energy sources. With the abundant energy from sunlight, solar cells have become prominent front runners in the renewable energy area. Doping of solar devices plays a crucial role in the fabrication of silicon solar cells as the process of generating electrical energy relies on separating electrons and holes efficiently at a p-n junction [66]. Research in this area primarily focuses on increasing the efficiency and lowering the fabrication costs of solar panels. One way to achieve a higher efficiency is to use micro- to nanometer-scale structures with larger surface to volume ratios and larger p-n junction areas. Such structures will adsorb more light and the electron-hole pairs will be more efficiently separated [67]. Radially doped silicon nanopillars and nanoholes have been reported by Puglisi et al. [49,50,68]. MLD was utilized to form a doped layer across the entire surface. The capability of MLD in forming junctions on non-planar surfaces makes it ideal for such applications.

5. Summary and outlook

MLD is a technique that employs dopant-containing organic molecules, grafting them onto a semiconductor surface by covalent bonding between the molecules and the substrate. A densely packed monolayer attaches the dopant onto the surface. Using a variety of dopant adsorbates allows to introduce dopants such as B, P, and As onto the substrate. Patterning of a dopant monolayer by selective etching has provided localized doping. The monolayer doping concept can also be extended to III-V semiconductors and has been used to dope these materials with sulfur or silicon.

A high-temperature annealing step drives the dopant into the substrate material. In this process, a capping layer is typically needed to prevent the dopant from escaping from the surface prematurely. Studies of MLD have not found carbon contamination to be an issue for the resulting electrical properties. A modified MLD process, monolayer contact doping (MLCD), relieves the substrate from the wet chemistry process for monolayer formation, which can help solving material compatibility issues.

The MLD has repeatedly shown the capability of doping ultra-shallow areas of less than 5 nm without causing crystal damage. This approach also allows the doping of 3-D structures. These advantages over ion implantation make MLD a promising alternative for the doping of future integrated circuits, particularly contributing to the trend of moving towards 3-D structures, for which doping by ion implantation encounters even more challenges. MLD has also been utilized to form a doped layer on the patterned surface of solar cells to achieve higher efficiencies and lower costs.

Acknowledgments

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