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

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A B S T R A C T

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. Terminal alkene (C=C) or alkyne (C≡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
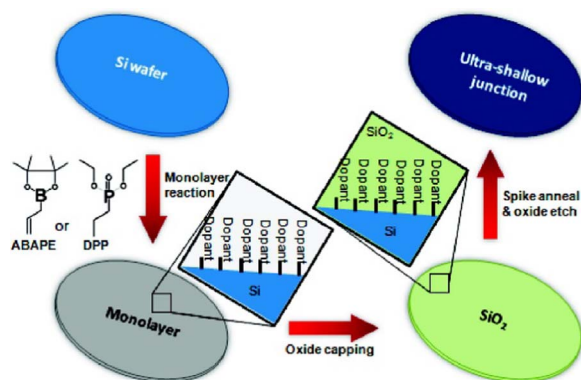
Fig. 1. Schematic representation of the monolayer doping (MLD) process. Figure adopted from Ref [3]. © 2009 American Chemical Society.
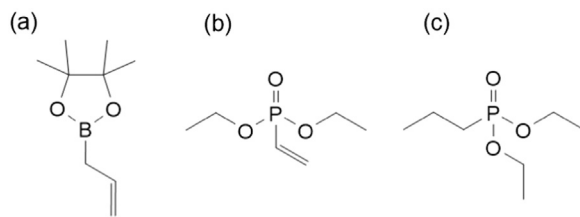

Fig. 2. Structures of the commonly used dopant adsorbate for MLD: (a) allylboronic acid pinacol ester (ABAPE); (b) diethyl vinylphosphonate (DVP); and (c) diethyl 1-propylphosphonate (DPP)..

(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 $8.3 \times 10^{14}\ cm^{-2}$, respectively [2]. This thus represents the maximum 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 $8 \times 10^{14}\ cm^{-2}$, 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.

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.