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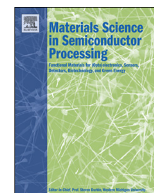

Effect of surface states on monolayer doping: Crystal orientations, crystallinities, and surface defects

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A B S T R A C T

Monolayer doping (MLD) has been regarded as the most suitable doping method for future semiconductor devices. MLD based on surface functionalization can be seriously affected by the surface states, including the orientations, crystallinities, and defects. We report for the first time the effect of surface states on boron-MLD (B-MLD) process and discuss the applicability of MLD for a fin structures. Depending on the surface states, the monolayer formation reaction is restricted, which causes more than five-fold differences in the doping level. Therefore, the surface states should be gravely considered before applying MLD and are crucial constraints in the MLD process on non-planar structures that have different surface states depending on its structural position. The B-MLD process on as-cleaned (100) and (110) silicon surfaces provides doping levels of 4.69×10^{20} and 2.48×10^{20} atoms/cm^3, respectively. The MLD efficiency on the (110) orientation is degraded by insufficient reaction sites for the hydrosilylation reaction on the monohydride-terminated (110) silicon surface. Additionally, the surface damage interrupts the formation of a dopant-containing monolayer, causing a poor doping level and dose uniformity. Our research provides new insights into the development of wet-chemical doping methods for non-planar devices by studying the effect of surface states on MLD efficiency.

1. Introduction

Downscaling semiconductor devices below 20 nm causes serious problems in silicon-based planar devices because of short channel effects (SCEs) [1–4]. A promising method for restraining SCEs is the formation of highly activated ultra-shallow junctions (USJs) in the source/drain extension region. However, as the USJ is continuously shallower, severe challenges arise in the conventional doping process [5–9]. Instead of continuing the miniaturization using traditional scaling theory, means of the boosting density by changing the transistor geometry form horizontal to vertical have been developed. The advent of such non-planar devices has also caused technological difficulties in the doping process [10–12].

Therefore, an innovative doping technology that can non-destructively introduce dopant atoms into the crystal lattice with atomic accuracy and realize conformal doping of non-planar structures is urgently needed. Several new doping strategies, including atomic-layer doping and wet-chemical doping have been suggested [13–17]. Among the proposed doping techniques, the monolayer doping (MLD) method is considered the most suitable technique to meet the crucial requirements of next-generation doping [17–20].

MLD has strong advantages because of its roots in wet-chemical methods toward surface functionalization [17,21]. Unlike destructive conventional doping techniques, which use accelerated energetic species [8,9], MLD utilizes a covalently anchored dopant-containing monolayer on the surface [17]. The dopant atoms of the dopant-containing monolayer can mildly diffuse into the crystal lattice via an annealing process; therefore, MLD does not cause remarkable damage, and it enables shallower nanoscale doping [17,18]. Furthermore, many authors insist that conformal doping of non-planar devices can be readily achieved via MLD because dopant-containing molecules are attached to every face of the non-planar structures with same packing density [19,20].

However, the MLD technique utilizing organic dopant-containing molecule composed of oxygen, hydrogen, carbon, and dopant atom can cause carbon-related detects into silicon because the impurities can diffuse into silicon along with the desired dopant atom during the thermal annealing processes [21]. Furthermore, the MLD process that is strongly associated with the surface chemistry and chemical reactions can be seriously affected by the surface states. During the MLD process, dopant-containing monolayers are created by a hydrosilylation reaction between the hydrogen-terminated silicon surface (Si–H bonding) and labile dopant-containing terminal alkene (C=C boding) or alkyne (C≡C bonding) groups [22,23]. The hydrogen-terminated silicon surface is

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typically prepared by chemical etching with fluoride-containing solutions and the etched surface is constructed with diverse Si–H bonding structures that vary with respect to the crystal orientation, surface defects, and roughness [22–28]. Thus, such surface states critically affect the subsequent assembly of the dopant-containing monolayer, which drastically changes the doping efficiency and final doping profile. Since a non-planar structure inevitably has different surface states (e.g. orientation, defects, and crystallinity) depending on its structural position, the dopant-containing molecules are attached to each face of the non-planar structure with different packing densities. Therefore, the surface states can be crucial constraints for the conformal doping of non-planar structures via MLD and should be seriously considered before applying MLD. Nevertheless, the constraints related to the surface states have never been discussed, and the potential for the application of MLD in future semiconductor devices has received extensive attention without being sufficiently validated.

In this paper, we demonstrate the applicability of MLD for conformal doping of the fin structure by reporting for the first time the effects of surface states on the MLD process. The (100) and (110) silicon surfaces appearing in a (100)-oriented silicon fin structure were prepared; the top, side- wall, and bottom of a (100)-oriented fin structure exhibit (100), (110), and (100) crystal orientations, respectively. Damaged and damage-cured surfaces were also prepared on both orientations in order to confirm the effects of surface defects on the MLD efficiency. The MLD processes on these surfaces were systematically studied to verify the effects of the surface states on the formation of the dopant-containing monolayer and the MLD efficiency. By precisely analyzing the effects of the surface states, especially of crystal orientations, crystallinities, and surface defects, in MLD, our research provides the insight needed to overcome the drawbacks of the wet-chemical doping methods for non-planar structures and can help to establish conformal nanoscale doping strategies.

2. Material and methods

2.1. Materials

Allylboronic acid pinacol ester (ABAPE, 97%) and, mesitylene (97%) were purchased from Sigma-Aldrich and used without further purification. Single crystal silicon wafers (4-in. n-type, prime grade) with a (100) orientation and resistivity of 1–10 Ω cm were prepared. The same type of silicon wafers with the (110) orientation were also prepared. These wafers were diced into 2 × 2-cm^2 pieces, cleaned in a piranha solution (H_2SO_4: H_2O_2 = 4:1, 100 °C) for 30 min, rinsed with deionized (DI) water, and finally dried in a stream of N_2.

2.2. Preparation of various surface states

Four different types of surface states (i.e., as-cleaned, damaged, damage-cured with thermal re-oxidation and an etching process, and damage-cured with a Standard Clean-1 (SC-1) treatment) were prepared on each of the (100)- and (110)-oriented silicon wafers. The as-cleaned surface refers to the surface immediately after the surface cleaned with the piranha solution. The damaged surface was fabricated using an STS Multiplex inductively coupled plasma dry etch system. The etch damage was induced on the as-cleaned surface by reactive ion etching (RIE) using HBr (40 sccm) and O_2 (2 sccm) at 3 mTorr of pressure with a DC power of 900 W and RF bias of 80 W. Some of these damaged surfaces were oxidized in a tube furnace at 1000 °C under a pure O_2 stream for 3 min and subsequently dipped in a buffered oxide etchant (BOE) for 3 min to strip off the 35-nm SiO_2 layer. Other damaged samples were cured using an SC-1 treatment (NH_4OH: H_2O_2: H_2O = 1: 1: 5) at 80 °C for 10 min. After the curing procedure, the samples were removed, rinsed with acetone, isopropyl alcohol (IPA), and DI water, and subjected to N_2 blow drying.

2.3. Grafting of dopant-containing molecules on the silicon surfaces

All chemical manipulations for the MLD process were carried out in a glove box in a dry and oxygen-free Ar environment. ABAPE (50 mL) was dissolved in mesitylene (200 mL) to make a 25% v/v solution, and this precursor solution was stored in a clean reaction flask for 12 h for stabilization. The previously prepared samples were immersed in a BOE for 2 min to remove native SiO_2 and to yield a hydrogen-terminated surface. After rinsing with DI water and drying under a N_2 stream, the hydrogen-terminated samples were immediately transferred into the precursor solution. Then, the reaction flask was covered with Parafilm and the hydrosilylation reaction that grafts the dopant-containing molecules onto the hydrogen-terminated surface was performed by heating the solution on a hotplate at 120 °C for 2.5 h. The reaction was stopped by removing the heat. The samples were then taken out and rinsed three times with IPA and DI water, which was followed by sonication in acetone for 5 min to remove any physisorbed material. Finally, the samples were rinsed again with DI water and dried carefully under a stream of N_2. These samples were kept under an inert atmosphere in a desiccator before further processing and analysis.

2.4. Capping layer deposition and annealing

A capping layer of SiO_2 was electron-beam evaporated onto the surfaces modified with a dopant-containing monolayer to prevent the escape of the dopant atoms from the surface and into the atmosphere during the subsequent annealing step. This surface was annealed under an N_2 atmosphere to drive the dopant atoms into the Si substrate. An electron beam was applied on the SiO_2 target using a SNTEK MEP-5000 electron beam evaporator system, resulting in a 50-nm-thick SiO_2 capping layer deposited with a deposition rate of ~ 2.3 Å/s. High-temperature annealing was performed at 950 °C over 10 s using an SNTEK RTP-5000 rapid thermal annealing processing (RTP) system. After annealing, the SiO_2 capping layer was removed in BOE over 3 min. The entire MLD process is schematically shown in Fig. 1.

2.5. Characterization methods

Scanning electron microscopy (SEM) imaging was performed using a JEOL JSM-7100F microscope operating at 15 kV. The surface morphology was investigated using atomic force microscopy (AFM, Park Systems XE-100). Transmission electron microscopy (TEM) images were acquired on a JEOL JEM-ARM200F microscope operating at an accelerating voltage of 300 kV. The surface crystallinity was examined using a Rigaku SmartLAB X-ray diffraction (XRD) system with a tube voltage and current of 40 kV and 30 mA, respectively. The X-ray diffractograms were scanned over the angular range of 10–85° (2θ) with a step length of 0.02° (2θ). A quantitative composition analysis of the dopant-containing monolayer was undertaken using X-ray photoelectron spectroscopy (XPS). The XPS spectra were acquired on a ThermoFisher Scientific K-Alpha ESCA system. Survey scans were acquired between 0 and 1350 eV with a step size of 1.00 eV, dwell time of 0.5 s, and pass energy of 200 eV. Core-level scans were carried out at the applicable binding energy range with a step size of 0.1 eV, dwell time of 0.5 s, and pass energy of 50 eV, averaged over 20 scans. All spectra were acquired at a takeoff angle of 90° with respect to the analyzer axis. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) dopant profiling was performed using an IONTOF TOF.SIMS 5 spectrometer with ${O_2}^+$ primary ions in the positive mode at an accelerating voltage of 1 kV and beam current of 239 nA. Quantification and depth calibration were based on reference samples with known profiles. ToF-SIMS analysis is a very useful method for the dopant profiling, but the first few nm of the profile was initially inaccurate and unstable due to the native oxide layer and non-equilibrium effects. The $^{30}Si^+$ signal as negative ions under ${O_2}^+$ bombardment incident during dopant profiling obviously showed the pre-equilibrium erosion regime at about

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