Microelectronic Engineering 149 (2016) 125–128

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Tunneling spectroscopy of p-type doping in silicon from boron-containing molecular monolayer

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ARTICLE INFO

Article history:
Received 20 May 2015
Received in revised form 14 September 2015
Accepted 3 October 2015
Available online 9 October 2015

Keywords:
Silicon
Surface doping
Diffusion
Transport simulation

ABSTRACT

Scanning tunneling spectroscopy was used to investigate surface doping in silicon, based on the grafting of a boron-containing molecular layer and the subsequent thermal diffusion of boron into silicon. Curve fitting of the experimental I(V) characteristics with a planar computation of the tunnel current yields a dopant concentration that is consistent with secondary ion mass spectrometry analyses in the subsurface region. Additional two-point probe electrical measurements performed at variable tip separations indicate a bulk-like transport, that corresponds to a significant diffusion of the boron impurities below the surface of low doped n-type Si wafers. Such results show the interest of multiple-probe scanning tunneling microscopy as a non-invasive technique to determine the electrically active content of doped layers during the fabrication of advanced integrated circuits.
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1. Introduction

Downscaling electronic components has led to the manufacturing of devices with lateral feature sizes in the tens of nanometer range. At this scale, incorporating dopant impurities in the semiconductor materials without creating structure defects is challenging [1]. Conventional approaches such as ion implantation or solid source diffusion suffer from crystal damages and a poor control over the dopant spatial distribution. In order to obtain junctions of better crystallographic and electronic quality, novel semiconductor doping techniques have been demonstrated. Most of them are based on the attachment of dopant-containing molecules at the semiconductor surface. When properly functionalized, the molecules can act as a gate, due to the formation of a dipole at the interface between the molecular film and the semiconductor crystals [2,3,4]. When the molecules contain dopant impurities, they can be thermally decomposed so that the impurities diffuse into a substitutional position in the semiconductor lattice. This mild approach has been coined as the molecular monolayer doping (MLD) method [5,6,7]. In this case, a precise control over the annealing process enabled the creation of electrical junctions in silicon [8].

As such a doping of the silicon crystal might occur on a very limited depth, characterizing its conductivity is very challenging. The probes of standard electrical characterization tools are usually very invasive and the measurements are subject to current leakages into the undoped or low-doped underlying layer [6,8]. Surface analysis techniques, such as the measurement of the surface photovoltage, seem to be more appropriate [8], but such a technique does not allow the change of the conductivity to be investigated at the scale of the fluctuations in the dopant distribution. In order to solve this issue and get insight into the electrical properties of doped Si substrates prepared through the MLD approach, it is important to assess the effectiveness of different surface science tools. Here, with scanning tunneling microscopy, we have investigated the electrical properties of p^+/n junctions that are prepared from the chemical grafting of an alkoxy borane compound [9]. Tunneling spectroscopy measurements of H-passivated Si surfaces reveals the p-type doping nature of the subsurface Si layer, once the molecules have been decomposed and the boron impurities incorporated into the material. When combined with numerical simulations of the tunneling current, we show that they provide valuable information on the doping level of the surface layer. In addition, conductivity measurements were performed with dual-probe scanning tunneling microscopy to highlight the significant extent of the doping layer below the surface.

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http://dx.doi.org/10.1016/j.mee.2015.10.002
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2. Experimental and simulation details

N-doped silicon wafers (10^{15} P·cm^{-3}) covered with a thin silica layer were partially dehydroxylated at 500 °C under high vacuum (10^{-5} mbar) for 12 h and stored in a glove box. The chemisorption of the molecular precursor was achieved by immersing the wafers in a 45 mL-toluene solution containing phenanthro[9,10-d]-1,3,2-dioxaborole for two hours in a glove box, affording self-arranged boron-surface species as depicted in Scheme 1 [9]. Diffusion of boron in the silicon matrix was subsequently performed by rapid thermal processing (RTP): the wafers were placed in a furnace filled with a low-pressure of N_2 (200 sccm) and heated up to 985 °C at a rate of 10 °C·s^{-1}. The temperature was then maintained constant for 4 s and quickly raised to 1000 °C for 1 s before being cooled down to room temperature.

Secondary ion mass spectrometry (SIMS) analyses were performed on samples previously etched using a vapor of hydrofluoric acid. As for the electrical measurements, they were carried out in an ultra high vacuum (UHV) system (base pressure lower than 5×10^{-10} mbar), which was equipped with a multiple-probe scanning tunneling microscope (STM) combined with a scanning electron microscope (SEM) (Nanoprobe, Omicron Nanotechnology) [10]. W tips were prepared by an electrochemical etching in NaOH and thoroughly cleaned in UHV by passing an electrical current through the W wires [11].

Prior to the STM experiments, the native oxide on the sample surface was briefly etched with hydrofluoric acid or an aqueous ammonium fluoride solution degassed under nitrogen flow [12]. Such a treatment allows the passivation of the surface where all the Si dangling bonds are saturated with hydrogen. Making the surface chemically inert significantly reduces its contamination rate, what ensures stable and reproducible tunneling spectra in ultra-high vacuum. The current–voltage characteristics were measured at fixed tip-sample separations with a tunneling current setpoint about 1 nA to obtain a conductance dynamic range of the order of 1000. These measurements were repeated between ten and twenty times for signal averaging.

As for the measurements of the sample conductance, two tips in electrical contact with the sample surface were used. In that case, each feedback loop has to be disabled with switch units. These switch units provided alternative outputs that both were connected to source-measure units. Tips were sequentially approached to the sample surface by monitoring the current. As described in Ref. [10], the current first increases exponentially and then saturates when the contact is established. In order to determine the contact resistance, I–V curves were measured between one tip in contact and the sample that was grounded. Then the sample was electrically disconnected from the ground, so that the current ran between both tips only. Lateral tip positioning on the surface was achieved with the SEM, the tip being either tunneling or retracted depending on the extent of the tip displacement.

In order to assist with the interpretation of the spectroscopic tunneling measurements, the tunnel current produced by the tip near the passivated Si(100) surface was computed with the Semitip code [13,14,15,16]. Briefly, the tip-induced band bending was calculated with a finite-element method assuming a hyperbolic shaped probe tip at a typical distance of 6–7 Å from the Si(100) surface. The semiconductor was treated in an effective-mass approximation and tunnel currents were computed using the Bardeen method. The computation involved the Si bulk-like states and did not take into account the contribution of surface states, since they are passivated with hydrogen. It assumed a spatial homogeneity in the doping concentration in the direction normal to the surface. The parameters in the computation were the tip radius-of-curvature, the contact potential (difference in work functions of tip and sample) and the doping level in the semiconductor.

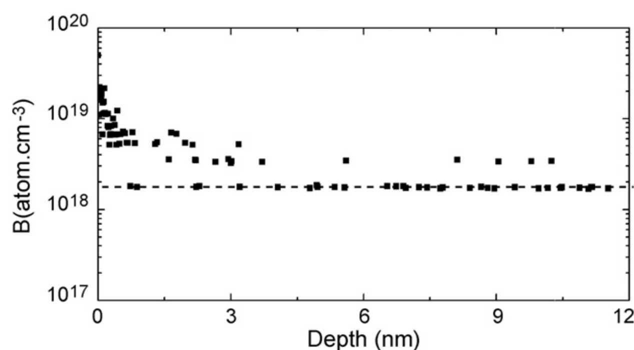
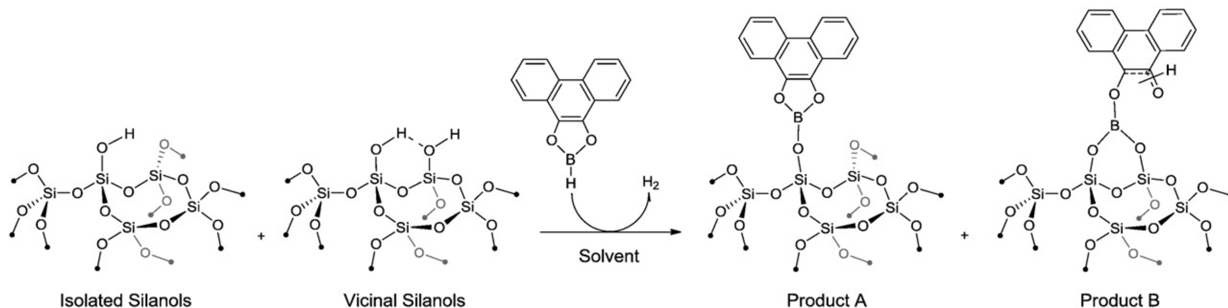


Fig. 1. Secondary ion mass spectrometry (SIMS) depth profile of boron obtained after rapid thermal processing of an n-type doped Si wafer grafted with the boron precursor. Primary ions: O_2^+. Impact energy: 500 eV. The background concentration is highlighted by the dotted line.

3. Results and discussions

The SIMS analysis (Fig. 1) of the boron-doped Si sample reveals that boron readily diffuses into the Si matrix after RTP. From the initial boron content grafted on the native oxide surface and quantified by vapor phase decomposition (VPD) followed by inductively coupled plasma mass spectrometry (ICPMS) [17,18], it is found that 0.04×10^{14} B atom·cm^{-2} diffused inside the Si matrix over the first 12 nm. In order to demonstrate the electrical activation of the dopants, the surface of the wafer was first investigated with scanning tunneling spectroscopy. The spectra measured for the untreated n-type doped wafer (referred as control wafer) and the boron-doped sample are shown in Fig. 2. The position of the Fermi level at the surface of the samples is given by the zero bias. The comparison of the untreated and doped samples reveals an asymmetry of the I(V) characteristic with respect to the Fermi level, indicating different electrical behaviors.

For the control wafer, three regimes of tunneling current are observed (Fig. 2(a)). The strongest component of the current is seen at positive voltage and corresponds to the flow of electrons from the STM tip into the empty conduction band states. A second component exists in the range −1.5 to 0 V. Then a change of the slope in the current characteristic appears and a third component turns on, extending to



Scheme 1. Reaction of Phenanthro [9,10-d][1,3,2]dioxaborole with the native oxide of a Si wafer. Adapted from [9].

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