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Open questions in electronic sputtering of solids by slow highly charged ions with respect to applications in single ion implantation

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Abstract

In this article we discuss open questions in electronic sputtering of solids by slow, highly charged ions ("potential sputtering") in the context of their application in a single ion implantation scheme. High yields of secondary electrons emitted when highly charged dopant ions impinge on silicon wafers allow for formation of non-Poissonian implant structures such as single atom arrays. Control of high spatial resolution and implant alignment require the use of nanometer scale apertures. We discuss electronic sputtering issues on mask lifetimes, and damage to silicon wafers.
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1. Introduction

The development of electron cyclotron resonance (ECR) and electron beam ion trap (EBIT) ion sources in the 80ies has made beams of relatively slow ($v < v_0$), highly charged ions (SHCI) available for ion solid interaction studies [1,2] and a wide array of new collision phenomena has since been quantified where the interaction of ions with solids is dominated by the deposition of potential energy of highly charged ions. SHCI like Xe^{44+} or Au^{69+} relax into charge state equilibrium within a time of only about 10 fs following penetration of a solid. Di-electronic processes, i.e. autoionization and Auger transitions, in a transient hollow atom mediate this rapid relaxation. Due to the swift relaxation, deposition of potential energy occurs close to the sample surface. The deposition of potential energy is associated with intense electronic excitation of the surface near target volume and increased sputtering of material has been reported for several dielectrics (oxides and alkali halides) as well as for GaAs for very high ion charge states [3,4]. The term "potential sputtering"

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[2,3] has been used to refer to effects of potential energy deposition from SHCI, in order to distinguish it from electronic sputtering induced by electronic energy loss, e.g. of swift ($v \gg v_0$) heavy ions. We view "potential sputtering", i.e. electronic sputtering induced by deposition of potential energy from SHCI, as a subset of general electronic sputtering. This view is based on the notion, that, irrespective of the details of hollow atom formation and decay, which pose many intriguing basic atomic physics questions, SHCI essentially form large numbers of hot electrons in solids. These electrons excite target atoms and molecules and electron emission into the vacuum can leave a nano-scale volume charged. Mechanisms of electronic sputtering by SHCI are quite similar to those in swift heavy ion interactions with solids in that they are very materials specific (e.g. defect mediated through compound specific formation and decay of self trapped excitons or holes) and subject of ongoing controversial debates (e.g. thermal spike versus Coulomb explosion). Recent reviews of the state of these debates can be found in [3,4]. In this article we discuss issues of electronic sputtering by slow, highly charged dopant ions in the context of our development of a single ion implantation technique.

2. Experimental results and open questions

In single ion implantation, single ion detection with effectively 100% detection efficiency can be achieved when high secondary electron emission yields from SHCI are used for ion impact registration [5]. The electron emission is largely independent of the kinetic energy of SHCI, and increases for very low impact energies due to enhanced time for above surface relaxation [2]. Very low impact energies translate into shallow range profiles with minimal straggling. This becomes important in the formation of single atom devices with single dopant placements requirements below ±10 nm [6]. The layout of a prototype two ^{31}P atom test structure is shown in an SEM image in Fig. 1. Here, a pair of silicon nanowire single electron transistors (SET) is formed by electron beam lithography with a 100 keV electron beam

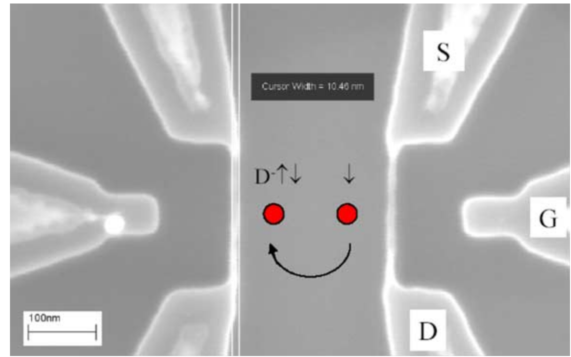

Fig. 1. Layout of a pair of silicon nanowire single electron transistors in SOI with positions of ^{31}P atoms (to be implanted) indicated for spin dependent charge measurements. The width of the silicon wire is 10.5 nm.

and an HSQ (hydrogen silsesquioxane) resist process. SETs are needed as sensitive electrometers for spin dependent charge transfer measurements, e.g. into the D^- state of a negatively charged phosphorus atom [6]. Control of the spin state of individual electrons is crucial for testing of proposed ^{31}P qubit device structures. In order to access the physics of the ^{31}P qubit in an all silicon, scalable architecture, we use single ion implantation to implant single P ions aligned to the nanowire SETs. We now discuss several critical issues of basic highly charged ion solid interaction in the context of this development.

The first critical issue when using highly charged dopants, such as $^{31}P^{q+}$ ($q = 12$ to 15), is whether the high charge state will lead to enhanced defect formation in the silicon matrix and consequently modified thermal budget requirements for damage repair and dopant activation through annealing. Sporn et al. [7] have shown strong preferential oxygen desorption for SHCI impacts on SiO_2 films. Charge relaxation times for SHCI are longer in dielectrics than in metals and semimetals due to the reduced availability of free electrons for screening of the transient hollow atom [8]. A 10 keV ^{31}P ion travels only a few nm during charge relaxation and the ~1.5 nm thick native oxide on silicon absorbs most of the initially deposited potential energy (9.3 keV for P^{15+}). The impact of single P^{15+} ions leads to enhanced emission oxygen from the oxide surface. Following

implantation, wafers are annealed for damage repair and dopant activation [5]. We are currently characterizing electrical properties of low fluence (<1E13 cm^{-2}), low energy (5–20 keV) highly charged P implants in silicon and silicon-on-insulator (SOI) [9].

The second issue when implanting highly charged dopant ions is their range profile as compared to that of singly charged ions. Pre-equilibrium energy loss enhancements [8] will compress range profiles at a given kinetic energy. In Fig. 2, we show magnetic sector SIMS depth profiles of low fluence (1E12 cm^{-2}) P^{12+} implants in silicon. The implant energies where 10 and 80 keV. A reduced ion range due to enhanced surface near stopping during charge relaxation requires very high resolution in depth profiling. For ^{31}P, magnetic sector SIMS is required in order to resolve ^{31}P from ^{30}SiH. Further, SIMS of top surface layers is hampered by beam–target equilibration effects and transients in relative sensitivity factors due to the changing chemical environment from the native oxide layer to bulk silicon. A cap oxide could be deposited prior to analysis, but this leads to enhanced beam induced mixing. Experiments with thin dielectric films and higher charged heavy ions can reveal the extend of pre-equilibrium stopping enhancements during low energy ion implantation [10].

Single ion implantation becomes interesting when individual dopant ions can be placed into regions with diameters < 10 nm and with high efficiency. The placement accuracy requirement is specific for the two qubit interaction scheme to be implemented [6,11]. Coupling by direct wave function overlap through exchange interaction requires qubit spacings of order 10 to 20 nm due to the Bohr radius of bound ^{31}P donor electrons in silicon. Coupling through spin coherent electron shuttling in a nuclear-electron spin encoding scheme relaxes the spacing requirement contingent to the magnitude of spin coherence lengths. Placement accuracy translates into placement resolution and alignment of the implant step. The placement resolution requires use of low energy ions, so that range straggling does not limit the placement accuracy. Further, diffusion during annealing has to be minimal [5]. We control the

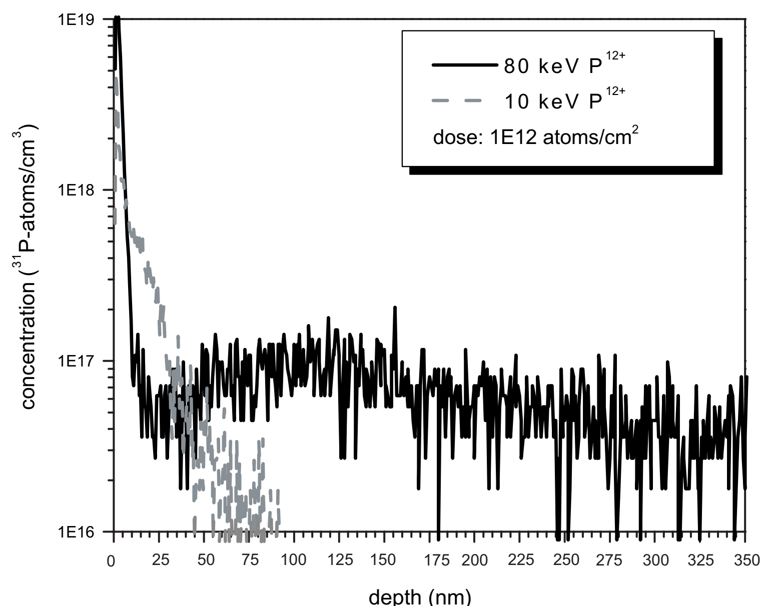

Fig. 2. Magnetic sector SIMS depth profiles of ^{31}P atoms in silicon wafers from implantation of P^{12+} ions with kinetic energies of 10 keV (dashed) and 80 keV (solid).

beam spot size on target through collimation of a focused beam in a small aperture. Very high alignment accuracy can be achieved by placing this aperture into the tip of an atomic force microscope (AFM) [12]. A schematic of our single ion implantation approach is shown in Fig. 3. Highly charged ions are extracted from an appropriate ion source (EBIT, or REBIT [13]) and reach the target station after momentum analysis in a double focusing analyzing magnet. The implant station is equipped with deflectors and electrostatic lenses that steer and focus the beam through the pre-collimator to the pierced AFM tip [14]. Fig. 4 shows a tip with hollow pyramid into which a 100 nm hole was drilled directly with a 30 keV Ga^+ beam in an FEI Strata 235 dual beam FIB. Hole diameters much below 100 nm are difficult to achieve in direct FIB drilling. In order to achieve the required placement accuracy, the spot size-limiting aperture needs to have a diameter < 10 nm. High aspect ratio (>4:1) holes with sub 10 nm diameters can be formed by thin film deposition over a larger hole [15]. In Fig. 5, we show a scanning transmission electron microscope line scan of Pt X-rays across the hole shown in the

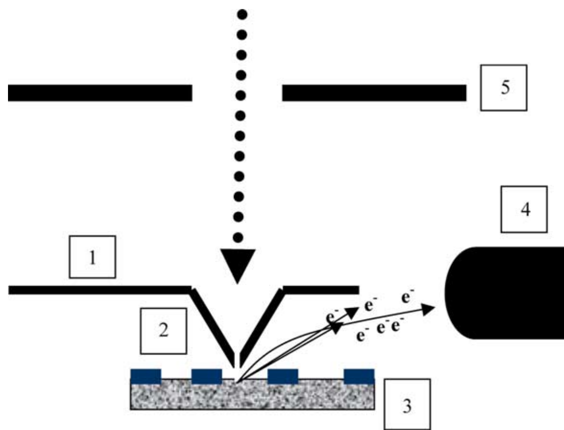

Fig. 3. Schematic of the single ion implantation setup with AFM alignment. 1: piezo-resistive AFM cantilever with hollow tip and small aperture (2), 3: high resolution sample stage and secondary electron detector (4), 5: pre-collimator.

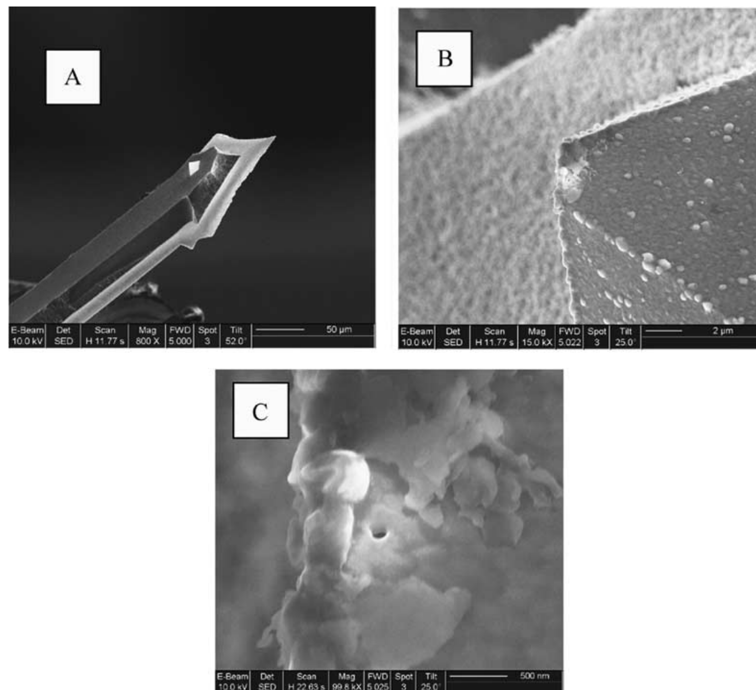

Fig. 4. Piezo-resistive AFM tip (A) with pierced, hollow metal pyramid (B), the hole in the pyramid has a diameter of about 100 nm (C).

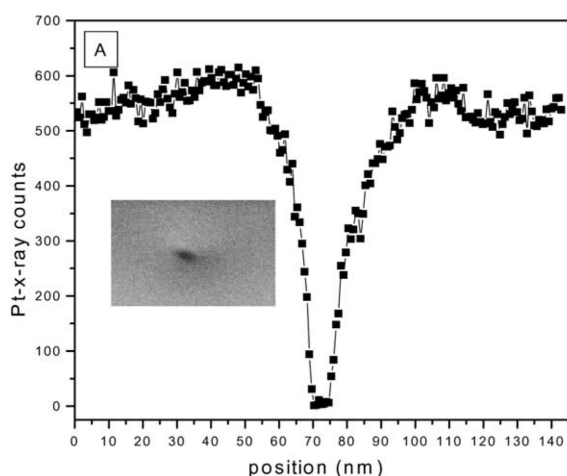

Fig. 5. STEM line scan of Pt X-ray intensities across a FIB drilled 100 nm wide hole following in situ ion beam assisted Pt deposition. The residual hole diameter is about 5 nm. The substrate was a 200 nm thick, low stress silicon nitride membrane.

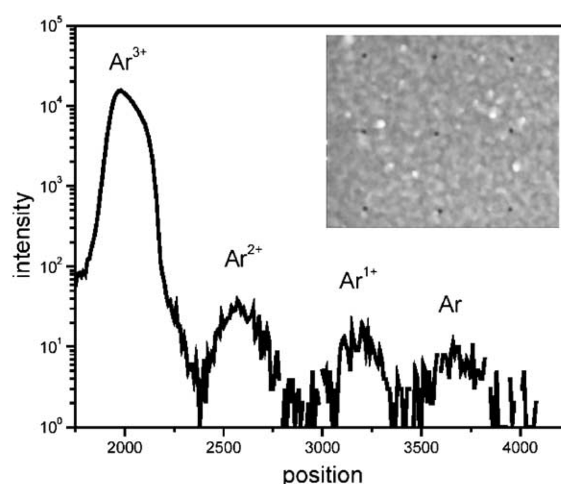

Fig. 6. Charge state distribution following transmission of Ar^{3+} ions ($E_{kin} = 9.6$ keV) through 30 nm wide holes in a 130 nm thick Ni membrane. An SEM image of the hole area on the membrane is shown in the insert.

insert. Here, a larger hole (∼100 nm diameter) had been drilled directly with the FIB beam into a silicon nitride membrane (200 nm thick). We then deposited a Pt film of several hundred nm thickness in the area of the primary hole by standard ion beam assisted thin film deposition. During thin film deposition, the hole closes and the hole diameter is reduced down to a value of about 5 nm.

It is now of great interest to see how such small apertures respond to exposure to SHCI and highly charged dopant ions. Clearly, charge state enhanced electronic sputtering will reduce mask lifetimes. However, electronic sputtering by SHCI has so far only been observed for dielectric films and some semiconductors, not for metals [16] and a metal coating can be applied to suppress electronic sputtering. A subtlety here is the recently reported effect of hole closing during beam exposure for Ar^{1+} ions. The balance of ad-atom formation and diffusion and material removal by sputtering can be adjusted with the target temperature and fluence rate to open or close small holes [17]. It can be expected that the optimal conditions for steady hole diameters are charge state dependent. Besides electronic sputtering, charge exchange is on important process in the interaction of SHCI with small apertures [18,19]. Transport of ions through ∼100 nm scale dielectric apertures has recently been reported by Stolterfoht et al. [19]. Here, charge exchange was found to be suppressed by channel wall charging even when collisions with capillary walls were forced by foil tilting. In Fig. 6, we show first data of charge state distributions for Ar^{3+} ion ($E_{kin} = 9.6$ keV) transmitted through 30 nm wide holes in a 130 nm thick nickel membrane on a silicon frame. Following hole transmission, exit charge states are separated in a electrostatic analyzer consisting of two parallel plates. Ions with different charge states are then detected with a position sensitive microchannelplate detector with resistive anode [1]. Data in Fig. 6 show horizontal lineouts of detected intensity distributions of transmitted ions. From a classical over the barrier model, the charge exchange fraction, f, can be estimated from the ratio of the critical radius for resonant electron capture from the channel walls, d, to the channel radius, r, $f \sim 2d/r$. The data for the rather low charge state Ar^{3+} show charge exchange fractions of only <1%, lower than expected from simple model predictions [20]. The critical radius for resonant electron capture form a 5 eV work function metal surface into an Au^{69+} ion is about 5 nm. It will be very

interesting to see charge exchange data for sub-10 nm capillaries and very highly charged ions, where critical radii for electron capture can approach channel diameters and to compare with detailed model predictions.

3. Summary

In this article we discuss open questions related to electronic sputtering of solids by slow, highly charged ions in the context of our development of a single ion implantation scheme with highly charged dopant ions. Results from fundamental studies in recent years provide important background data and point to experiments needed in order to quantify charge state effects on electrical properties of silicon implanted with highly charged dopant ions, electronic sputtering effect on beam collimator lifetimes and charge exchange processes in nanometer scale capillaries.

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