



Formation of Cu nanoparticles and Cu₃Si phase in Si by ion implantation

A.I. Gumarov^{a,b}, A.M. Rogov^{a,b}, A.L. Stepanov^{a,*}

^a Zavoisky Physical-Technical Institute, FCR Kazan Scientific Center of RAS, 420029, Kazan, Russia

^b Kazan Federal University, 420008, Kazan, Russia

ARTICLE INFO

Keywords:

Ion implantation
Copper nanoparticles
Copper silicide

ABSTRACT

The results of low-energy high-dose implantation of single-crystal *c*-Si by Cu⁺ ions at energy 40 keV, current density 8 μA/cm² and doses of 3.1·10¹⁶ and 1.25·10¹⁷ ion/cm² are presented. It was shown that if the dose is low Cu nanoparticles with average diameter of 10 nm are formed in a near-surface implanted Si layer. When the dose is higher Cu ions chemically interact with the Si atoms and the synthesis of the η'-phase Cu₃Si instead of Cu nanoparticles is observed. Cu nanoparticles transformation to Cu₃Si phase in the sample heated by long time implantation is discussed.

1. Introduction

In practice order to create various microelectronic devices based on Si combined with Si-silicide precipitates, implantation of Si substrate by transition metal ions such as Fe⁺, Co⁺, Ni⁺ and Cu⁺ is effectively used [1,2]. However, the implantation of Si by Cu⁺ ions was far less studied in this context. Apparently the first publications on Cu⁺-ion implantation of *c*-Si at energies $E = 70$ and 150 keV and doses $D = 2.0\text{--}5.0 \cdot 10^{15}$ ion/cm² were presented in 1978 [3] and 1980 [4]. Those implanted layers were then annealed using nanosecond laser pulses or thermal treatment. After that the initial surface amorphous layer *a*-Si was completely recrystallized to *c*-Si structure and the implanted Cu was segregated out to the sample surface to give a channelled distribution of crystalline silicide phase. Late in the work [5], Cu⁺-ion implantation was applied for selective electroless Cu plating with D from $5.0 \cdot 10^{14}$ to $6.4 \cdot 10^{16}$ ion/cm² for energies (E) of 20 and 40 keV. Unfortunately, no discussions on the formation of any chemical composition with Cu and Si atoms exactly after the implantation was presented in this publication.

In practice metal impurities could degrade electronic device properties in Si dramatically even in small concentrations, below 10^{12} cm⁻³. Most transition metals in Si have high diffusivities and relatively low solubilities, therefore deleterious atoms are drawn from large distances in the bulk to trap or precipitate at suitable sites during annealing and/or subsequent cooling. The creation of impurity precipitation or trapping sites, the so-called gettering sites, by introduction of appropriate near surface flaws or defects was effectively applied to reduce the concentration of impurity metal in Si [6]. Recently it was shown [6–8], that

Cu is efficiently gettering to voids in Si preliminarily formed by H⁺ - or He⁺-ion implantation (H:Si and He:Si). For example, trapping of Cu atoms at internal voids (porous or cavities) and nucleation of Cu₃Si phase in the sample He:Si fabricated by Cu⁺-ion implantation for $E = 50$ and 100 keV at $D = 3.2 \cdot 10^{16}$ ion/cm² followed by thermal annealing at high temperatures was observed [7].

In general, as it is seen from the reviewed research [3–8] after Cu⁺-ion implantation of *c*-Si substrate followed with laser and thermal annealing Cu-silicide phase was only detected, and no Cu nanoparticle formation was observed. However, on the other hand, it is commonly known that during implantation of substrates with Si atoms such as silica and soda-lime silica glasses by Cu⁺-ions after accumulation of impurity in surface layer over solubility limit a nucleation and growth of metal nanoparticles occurred without any Cu-silicide phases [9–12]. Threshold D value for nucleation of Cu nanoparticle in glasses is about $1.0 \cdot 10^{16}$ ion/cm². Cu nanoparticles were also saved in glasses after thermal and laser annealing. Therefore, in the current study series samples were prepared at different D and they analyzed by scanning electron microscopy (SEM), Auger and X-ray photoelectron spectroscopy (XPS) to explore the key possibility for Cu nanoparticles formation in Si matrix by Cu⁺-ion implantation.

2. Experimental

As substrates *c*-Si (111) wafers with thickness of 0.5 mm were used. Implantation was carried out by Cu⁺ ions at $E = 40$ keV, with current density $J = 8$ μA/cm² and $D = 3.1 \cdot 10^{16}$ and $1.25 \cdot 10^{17}$ ion/cm² using the ion accelerator ILU-3 at room temperature of the irradiated substrates as

* Corresponding author.

E-mail address: aanstep@gmail.com (A.L. Stepanov).

<https://doi.org/10.1016/j.coco.2020.100415>

Received 5 May 2020; Received in revised form 5 July 2020; Accepted 13 July 2020

Available online 25 July 2020

2452-2139/© 2020 Elsevier Ltd. All rights reserved.