

Formation and Growth of Cu Nanocrystallite in Si(100) by Ion Implantation

H. K. Kim, S. H. Kim and D. W. Moon

*Surface Analysis Group,
Korea Research Institute of Standards and Science
P.O. Box 102, Yusong, Taejon 305-600, KOREA*

Abstracts

In order to produce Cu nanocrystallite in silicon wafer, the implantation technique was used. The samples of silicon (100) wafers were implanted by Cu^+ ions at 100 keV and with varying the doses at room temperature. Post-annealing was performed at 800°C with Ar environment. To investigate the formation of Cu nanocrystallite with ion doses and growth process by thermal annealing, SIMS and HRTEM (high resolution transmission electron microscopy) spectra were studied.

1. Introduction

During the last decade, nanocrystalline materials (typically having crystallite size of just a few nanometers) have been of much interest because novel properties appear in these materials, such as the enhanced plasticity of a nanocrystalline ceramic material and the high diffusivity of Ag in nanocrystalline Cu. Hence, nanocrystalline materials will be applied widely in technology.

In semiconductor device manufacturing, the metallization technique is

very essential element to use the interconnection, ohmic contact electrode, metal-semiconductor contact. But the adhesion problem between metal and semiconductor has to be solved. Nowadays to improve the adhesion between metal and semiconductor, thermal annealing method is used after deposition with physical or chemical vapor deposition. There are some disadvantages in thermal annealing method such as it has difficult process and different thermal conductivities between metal and semiconductor. To solve these disadvantages, ion implantation method is useful to obtain the metastable phase at room temperature.

In this study, in order to metallize in semiconductor, Cu ions were implanted into Si(100), because of Cu hardly react with Si. The main objectives of this article is the determination of the formation of Cu nanocrystallite with ion doses and growth process by thermal annealing.

2. Experimental procedure

Etch-polished (100) oriented n-type Si wafers were bombarded at room temperature. Ion implantation was carried out using a CHORDIS (Danfysik products, model 920-2) sputter version. The mass-selected ions ($^{63}\text{Cu}^+$) were implanted into silicon at the energy with 100 keV at dose 1×10^{16} , 6×10^{16} ions/cm². Current density of the copper ion beam was about 25 $\mu\text{A}/\text{cm}^2$. Sequential post-annealing was performed in different conditions in argon environment. To investigate the formation of Cu nanocrystallite with ion doses and growth process by thermal annealing, HRTEM and FT-IR spectra were studied.

3. Results and discussion

The SIMS depth profile shown in Fig.1 for samples implanted(a), and

annealed(b) at 800°C with 6.0×10^{16} ions/cm². The copper depth profile for silicon implanted at room temperature had a symmetrical shape. The copper depth profile for silicon annealed at 800°C changed in a parallel shape. It means that Cu atoms interdiffused into Si bulk side by thermal annealing.

Cross-sectional microstructures for Cu implanted at room temperature are shown in Fig. 2 and annealed at 800°C for 10 minutes and 1 hour in Fig. 3. For the as-implanted sample with 1.6×10^{16} , 6.4×10^{16} ions/cm², the surface top layer (namely, native oxide layer) was very thin (about 1.5 nm) and smooth. The buried amorphous layer was thick (about 125 nm). The copper clusters existed in the buried amorphous. Implanted copper causes considerable damage to a substrate, and changes crystalline Si into amorphous, since crystalline Si cannot maintain its crystalline state at room temperature. The average size of the copper cluster is measured with 3.65 nm for 3.0×10^{16} ions/cm², and 5.24 nm for 6.4×10^{16} ions/cm² in as-implanted state. We couldn't be measurable for 1.6×10^{16} ions/cm² because of small size of it. With increasing the annealing time at 800°C, the buried amorphous layer easily changes to the crystalline state. The dissociation of the copper atoms to the amorphous silicon substrate enhances the inhomogeneity and instability of the amorphous region. During the annealing process the formation of stacking fault induces copper mobility which precipitates in defects. For the annealed state the copper distribution is located closer to the defect distribution than to the expected ion profile as calculated by TRIM. The reconstruction of Si-Si bondings is chemically favoured, so the copper atoms which are not chemically bound to substrate atoms diffuse and form clusters. These copper clusters also easily cause the growth between copper clusters because of the inhomogeneity of concentration in buried amorphous layer. Therefore, copper cluster finally grow into about 20 nm near the surface, about 8 nm near the interface between buried amorphous layer and crystalline silicon region.

For the as-implanted state with 6.4×10^{16} ions/cm² the copper clusters are

very close or superposed, while the average distance between clusters is small and Ostwald ripenings are clearly observed above 1.6×10^{16} ions/cm². For higher the copper ion with 6.4×10^{16} ions/cm², although coalescence is favoured compared to the Ostwald ripening process, the latter was observed unambiguously in this experiment. To separate clearly coalescence and Ostwald ripening stereographic analysis are at present analyses are at present underway.

4. Conclusion

Cu ion implantation were performed into silicon(100) and investigated the formation of Cu nanocrystallite with ion doses and growth process by thermal annealing. The implanted Cu cluster size is increased as amount of implanted Cu ion doses.

During the annealing process the formation of stacking fault induces copper mobility which precipitates in defects. These copper clusters also easily cause the growth between copper clusters because of the inhomogeneity of concentration in buried amorphous layer. Therefore, copper cluster finally grow into about 20 nm near the surface, about 8 nm near the interface between buried amorphous layer and crystalline silicon region.

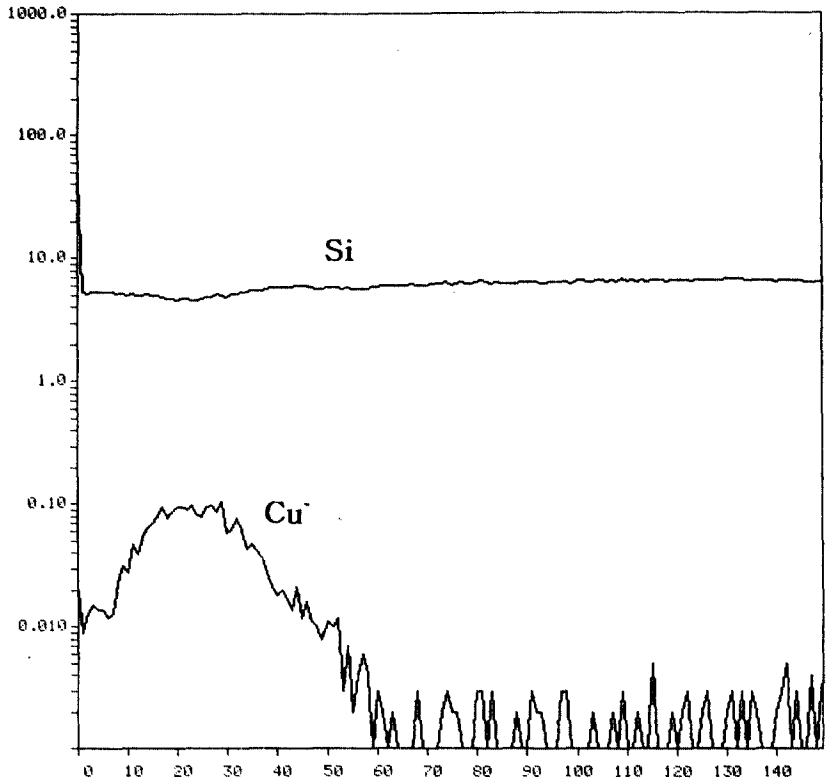


Fig. 1(a). SIMS depth profile of Cu implanted Si(100) with ion dose 6×10^{16} ions/cm².

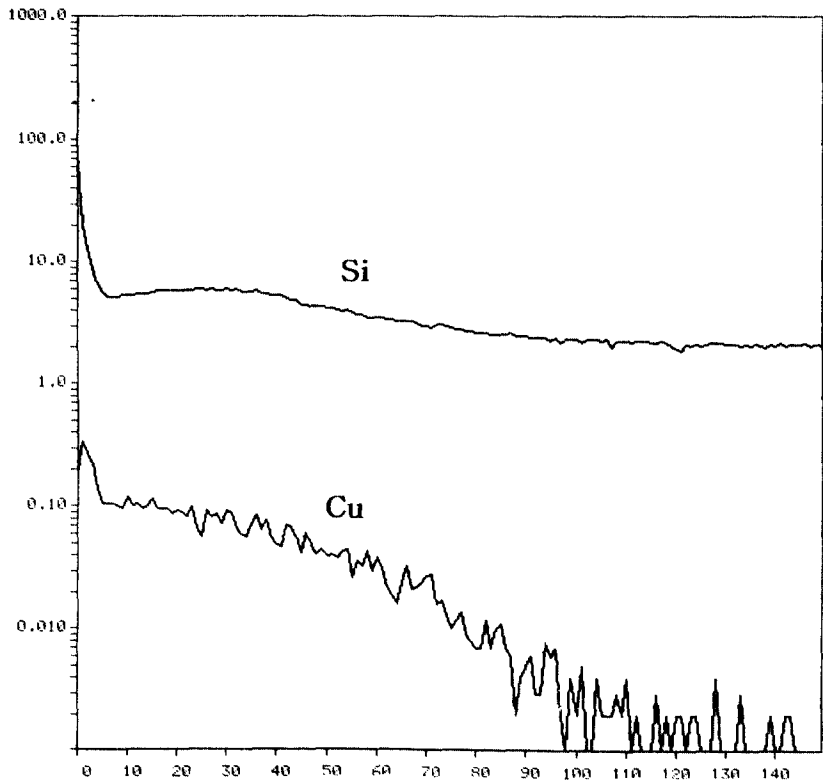


Fig. 1(b). SIMS depth profile of Cu implanted Si(100) with ion dose 6×10^{16} ions/cm² after annealing at 800°C in 4 hours.

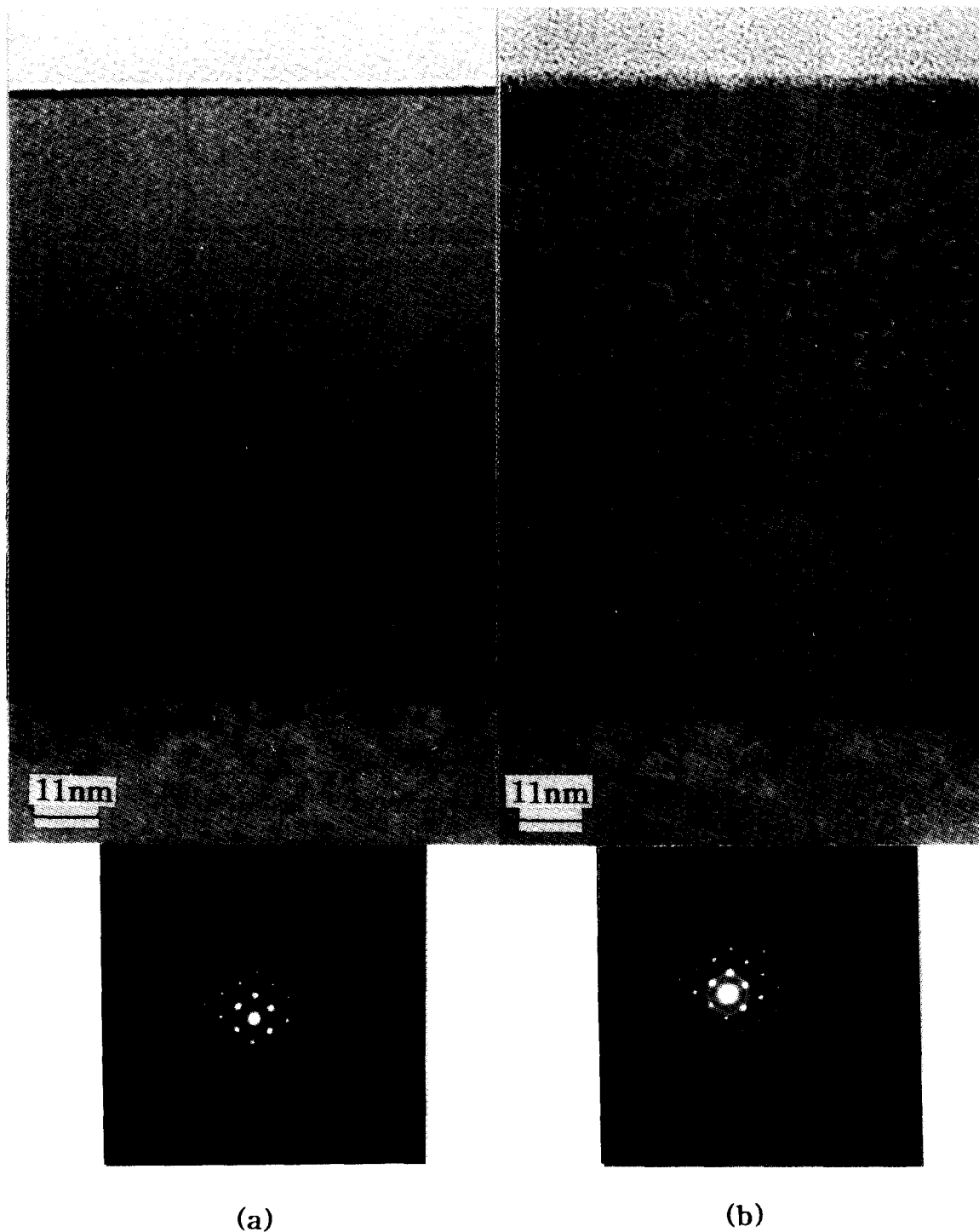


Fig. 2. Cross-sectional microstructures of Si wafers for Cu implanted with ion dose with (a) 1.6×10^{16} ions/cm², and (b) 6.4×10^{16} ions/cm² at room temperature.

1.6×10^{16} ions/cm²

6.4×10^{16} ions/cm²



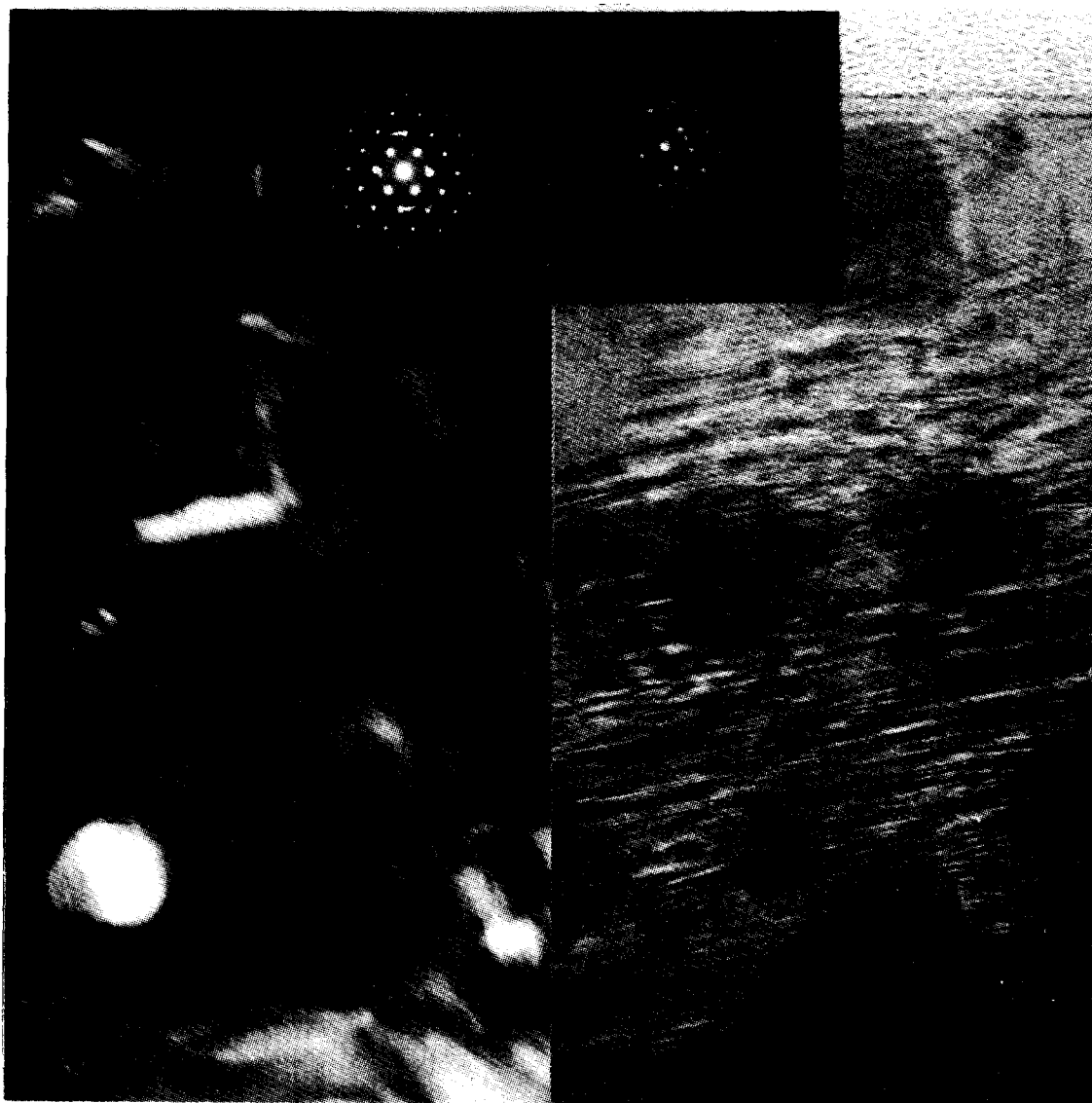
bright field image

dark field image

Fig. 3.(a) HRTEM images after annealing at 800°C in 10 minutes.

1.6×10^{16} ions/cm²

6.4×10^{16} ions/cm²



bright field image dark field image

Fig. 3.(b) HRTEM images after annealing at 800°C in 1 hour.