

Metallic Impurity Growing Behavior on Surface Crystal Structure

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Metallic impurity growing behavior on surface crystal structure has been investigated. The study reveals that the growing behavior of metallic impurity depends on substrate. Contamination level is independent of substrate. However, Cu particles on a-Si surface have not been observed by using SEM. Cu impurity level on c-Si is reduced by 2 orders by using sulfuric acid-hydrogen peroxide mixture (SPM) cleaning. In case of a-Si surface, the SPM cleaning is not effective. Our experimental results suggest that a-Si contains, although total Cu amount is equivalent, more partial Cu impurities under the surface. They exist in direct bonding with Si and/or in the native oxide layer.

1. Introduction

As semiconductor devices are scaled down, ultraclean Si surface is essential for device integrity. It is well known that metallic contamination on the Si surface is fatal to semiconductor devices.¹ Metallic contamination increases leakage current at P-N junction, decreases oxide breakdown voltage, and reduces minority-carrier lifetime. Therefore, removal efficiency of the metallic impurity is further required to reduce metallic contamination level below detection limit. It has been reported that metals with low redox potential, such as Fe and Ni, do not form any chemical bond with Si substrate and can be removed easily from Si substrate by wet cleaning.² On the other hand, noble metals with high redox potential, such as Cu, Ag, and Au, form a chemical bond with Si and are quite difficult to remove from the surface by using conventional cleaning. Many articles discussed the particle growth mechanism of noble metals such as Cu.³

Since a-Si is widely used in forming channel Si of thin film transistor liquid crystal display (TFTLCD) and interconnects in ultra large scale integrated (ULSI) circuits, understanding metallic impurity growing behavior on a-Si is important. In order to understand cleaning mechanism of metallic impurity, we have investigated the metallic particle growing behavior on surface crystal structure, and the results are presented in this article.

2. Experimental

An a-Si (a-Si stands for *in-situ*

phosphorus doped amorphous Si) film was deposited at 510°C on thermally oxidized Si wafer in a hot wall LPCVD vertical system with Si₂H₆ and PH₃ (1% diluted with N₂) gases. A c-Si (N-type, 7 ~ 12 Ω cm : c-Si stands for single crystal Si) wafer was used as a reference. The native oxide grown during SPM pre-treatment cleaning was etched off by 1 min. dip in a 0.5% dilute HF solution.

The Cu concentration in CuF₂ solution was set at 1 ppm independent of surface crystal structures. Samples were dipped for 3 min., rinsed for 10 min. in the UPW and dried using ultra pure nitrogen gas. The metallic concentration level on the substrate was measured by Total Reflection X-ray Fluorescence (TRXRF) with incident angle of 0.05 degree and X-ray excitation of 30 KV and 200 mA. Surface morphology after contamination was observed by Scanning Electron Microscopy (SEM) with normal incidence angle (90 degree). Finally, X-ray Photoelectron Spectroscopy (XPS) for native oxide thickness measurement was carried out in a Scienta ESCA-300 system with monochromatic Al-Kα and acceptance angle of 3.3 degree. Take-off angle was adjusted to 15 degree and yield of Si_{2p3/2} was fixed above 10⁵ Count Per Second (CPS).

3. Results and discussion

Fig. 1 shows the amount of Cu adhered on c-Si and a-Si surface after contamination. When a-Si surface is contaminated in Ultra Pure Water (UPW), contamination level has no difference from that of c-Si. From SEM images in Fig. 2, the number of Cu particles per unit area on c-Si is correlated with the TRXRF results.

However, Cu particles on a-Si surface were not observed. These results suggest that the growing behavior of Cu particle on a-Si be quite different from that on c-Si. Fig. 3 shows that the amount of Cu contamination on the c-Si and a-Si in CuF₂ solution with 1ppm Cu spiked as a function of dipping time. The amount of Cu impurities on the a-Si for 1 second dipping is about 10 times higher than that on the c-Si. The a-Si surface is expected to have many defect sites like steps and kinks, which may be chemically activated for the formation of Si-OH or Si-O during UPW rinse before contamination.^{3,4,5,6} In the early stage of contamination, contamination level is known to be determined by the number of defect sites.⁷ Different contamination behavior between c-Si and a-Si can be attributed to the difference of the number of defect sites where the surface is not hydrogen-terminated. In the early stages, because the number of nuclei on the c-Si surface are low on the a-Si surface, Cu nuclei on c-Si can grow easily by Brownian motion within the contamination time.² On the other hand, the high density of nuclei on a-Si can restrict the Brownian motion and Cu particles may be too small to be observed by SEM measurement. (Sometimes, very small particles were observed.) The differences in the number of nuclei on surface crystal structure can explain the contamination level as shown in Fig. 1 and the number of particles as shown in Fig. 2.

Fig. 4 shows the removal efficiency of metallic impurities on various Si substrates after sulfuric acid-hydrogen peroxide mixture (SPM, H₂SO₄:H₂O₂ = 4:1) cleaning. Cu impurity contamination on c-Si was reduced to the order of 10¹² atoms/cm² by SPM cleaning. Cu impurities on a-Si, however, are rarely removed by SPM cleaning. Fig. 5 shows the relationship of SPM cleaning efficiency and native oxide thickness grown intentionally before contamination. It is worth noting that the Cu contamination on a-Si is also removed by SPM cleaning in comparison with the result of Fig. 4. SPM cleaning with high redox potential value was reported to have a good cleaning efficiency to Cu contamination on native oxide⁸. From our result, it is clear that the Cu impurities contamination on a-Si compared to that on c-Si have the characteristics of direct bonding on Si as well as the existing inside of native oxide. In case of Cu impurities in native oxide and direct bond on Si, the SPM cleaning is not effective although it has high redox potential value.

In summary, the difference of the number of surface defect sites leads to

increase of initial contamination level on a-Si surface. The increase of initial contamination level on a-Si in comparison with that on c-Si results from the direct bonding of Cu ions to Si and the existence of Cu in the native oxide. As a result, SPM cleaning is not effective on a-Si surface.

4. Conclusion

The growing behavior of metallic impurities on surface crystal structure was investigated. When the sample is contaminated in the UPW, Cu contamination level on c-Si and a-Si shows no difference. From the SEM images of a-Si surface, however, Cu particles are not observed on a-Si. Cu impurity level on c-Si surface is reduced by 2 orders using SPM cleaning. In case of a-Si surface, the SPM cleaning is not effective; however, when native oxide is pre-existed on the a-Si surface before contamination, the SPM cleaning is effective in removing Cu impurity. From our result, it is clear that the Cu contamination on a-Si compared to that on c-Si has the characteristics of direct bond with Si as well as the existence in native oxide. We believe that this result is directly related to the wet cleaning efficiency.

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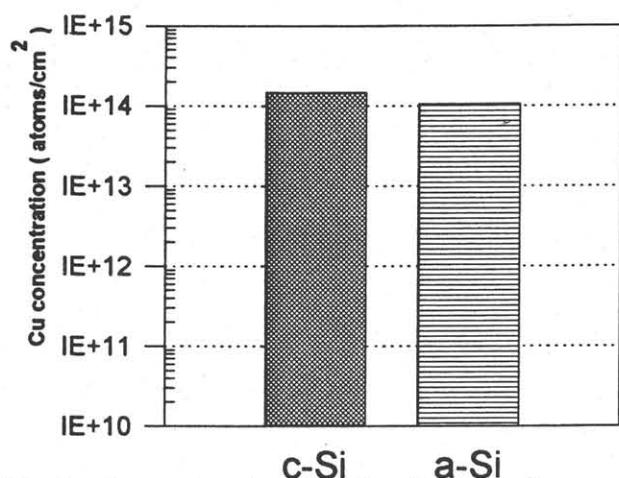


Fig.1 Cu contamination level on surface crystal structure [with Cu : 1 ppm, 3 min].

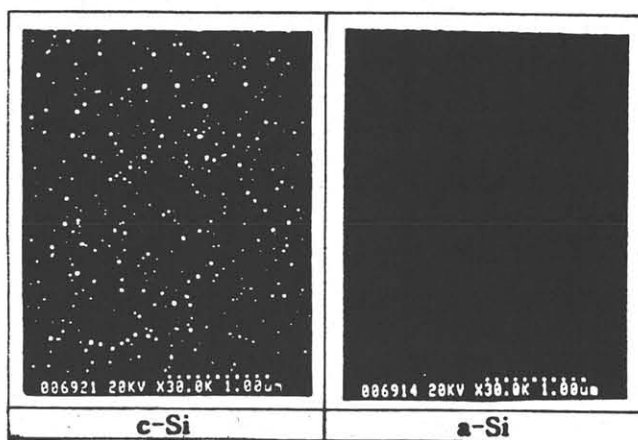


Fig.2 SEM images after contamination [with Cu : 1 ppm, 3 min].

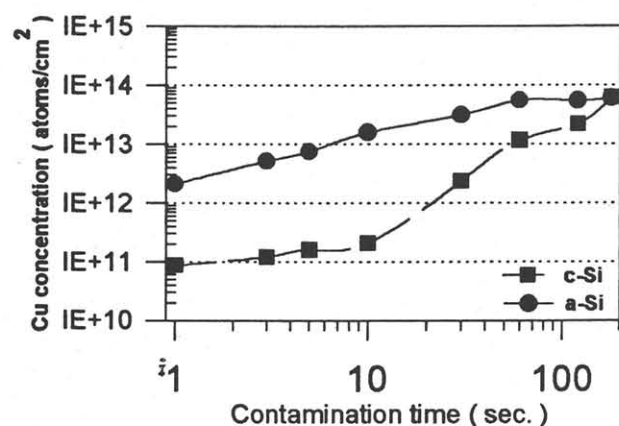


Fig.3 The amount of Cu adhered as a function of contamination time [with Cu : 1 ppm].

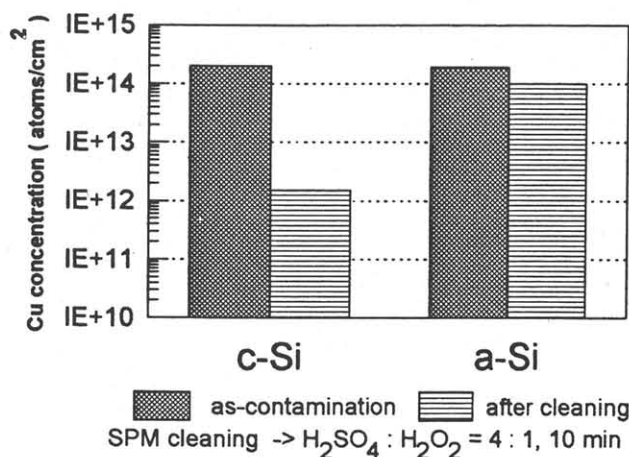


Fig.4 SPM cleaning efficiency [with Cu 1 ppm, 3 min.].

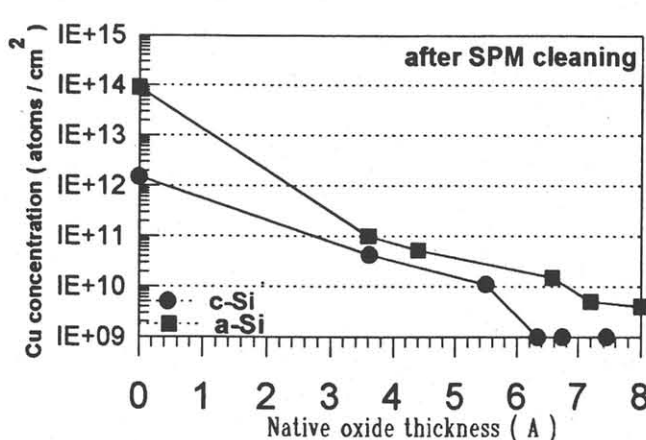
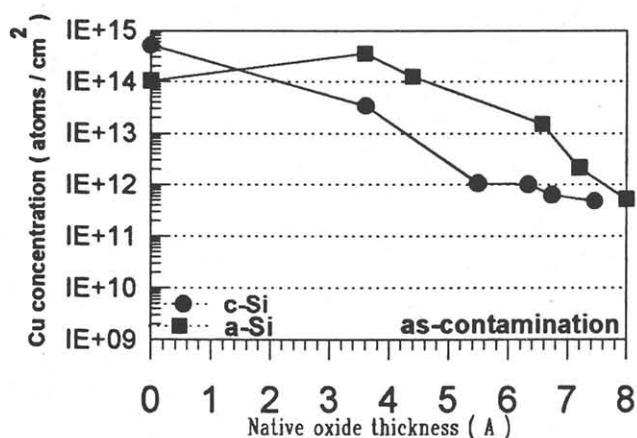


Fig.5 The relationship of SPM cleaning efficiency and native oxide thickness intentionally grown before contamination [with Cu 1 ppm, 3 min.].