

Backside gettering of Cu by porous Si

S. Roorda, B. Morin, E. Soudée, and S.C. Gujrathi

Abstract: Porous Si can act as a getter for Cu. In this experiment, Cu was deposited on the front surface of a Si wafer, after a part of the back surface of the same wafer had been rendered porous. Following a vacuum anneal treatment (900°C, 2 h), ion scattering shows that some Cu has diffused through the Si wafer and that up to 0.8×10^{16} atoms cm^{-2} can be gettered in the porous Si layer opposite the deposited Cu.

Résumé : Le Si poreux peut servir de piège pour le Cu. Dans cette expérience, nous avons déposé du Cu sur la surface d'une pastille de Si, dont une partie du côté opposé a été rendue poreuse. Nous avons montré par analyse de faisceau d'ions qu'après un recuit (900°C, 2 h) sous vide, une partie du Cu a traversé la pastille et que 0.8×10^{16} atomes cm^{-2} peuvent être piégés dans la couche de Si poreux.

Introduction

Gettering [1] of metal impurities is an effective method of improving carrier lifetime and mobility in the near-surface layers of Si wafers that are to be used as starting material for micro-electronic [2] or photovoltaic [3] devices. Gettering involves a source (e.g., Cu impurities present at sub-ppm levels in Si wafers), a thermal anneal (to release the impurity from its site in the bulk and to allow it to diffuse), and a sink. This sink may be a structural or chemical defect inside the wafer but outside the active zone (intrinsic gettering) or the surface of the wafer (extrinsic gettering). Structural defects acting as a sink for impurities may be generated mechanically [4] or by ion implantation in the back [5] or front [2, 6] surface of the Si wafer.

Recently, a new, intrinsic sink has been found to be a candidate for efficient gettering. Nanometre-sized microvoids, introduced by He-ion implantation in Si, have been shown to getter Cu [7]. The microvoids are formed when the ion-implanted He vastly exceeds its solid solubility in Si and forms tiny bubbles. A high-temperature anneal treatment drives out the He and leaves the microvoids behind [8]. It was found [7] that up to 10^{16} atoms cm^{-2} can be gettered and that the binding energy of Cu in such microvoids (the depth of the sink) is larger than that of Cu in Cu_3Si . This suggests that another sink could exist, which would be an extrinsic one, namely, the large and strongly curved surface of porous Si. Porous Si is a microscopic spongelike structure that can be made by electrochemical attack of monocrystalline Si [9]. It has recently received much attention because of its luminescence properties. Here, we show that porous Si can indeed getter Cu.

Sample preparation, gettering, and analysis techniques

Small regions of porous Si were prepared on the backside of

double-sided polished Si wafers as follows. Al was vacuum deposited on the front surface of a p-type, $1\text{--}10 \Omega \text{ cm}$, $\langle 100 \rangle$ Si wafer to serve as an electrical contact during the electrochemical attack. An area of 7 mm diameter on the backside was etched for 6 s in an HF–methanol–ethanol mixture using a current density of 26 mA cm^{-2} , resulting in approximately 100 nm of porous Si. After the electrochemical etch, the samples were dipped in 10% HF aqueous solution to remove the Al contact.

A layer of approximately 80 nm of Cu was deposited on the front surface of the same Si wafer by RF plasma sputtering. The base pressure of the sputter system was 2×10^{-7} mbar (1 mbar = 0.1 kPa). (In an earlier stage of the experiment, Cu layers were deposited by thermal evaporation in a diffusion pumped bell jar with a base pressure of 5×10^{-6} mbar.) Immediately before loading in the vacuum system, the samples were again subjected to an HF dip. On some samples, half of the front surface was masked so that one part of the porous Si was opposite the Cu layer while the other part was opposite a clean Si surface. Some samples were not exposed to Cu at all and kept as a reference.

After Cu deposition, some samples were put aside for ion beam analysis. Other samples were annealed in a vacuum of 10^{-6} mbar. Two anneal treatments were applied. The first one, at 600°C, allows the Cu to react with the Si surface, forming Cu_3Si , while some of the oxygen is removed from the porous Si layer. The second anneal, 2 h at 900°C, allowed some of the Cu to diffuse through the Si wafer (the diffusivity of Cu in c-Si at 900°C is $2.5 \times 10^{-4} \text{ cm}^2$) and become trapped in the porous Si.

Two ion-scattering techniques were used for the analysis of the samples after the anneal treatments: Rutherford backscattering spectroscopy [10] (RBS) and elastic recoil detection in conjunction with time-of-flight [11] (ERD–TOF). For RBS, scattered Li ions of incident energy 3 MeV were detected at 157.5° with a solid state detector. For ERD–TOF, the sample normal was tilted 85° with respect to a 30 MeV Cl beam while being held coplanar with the incident and detected beam. The detection system, consisting of a thin C foil, a flight tube, and a surface barrier detector, detected recoils scattered at an angle of 30° with respect to the incident beam. ERD–TOF is a coincidence technique that determines for each recoiled ion both the velocity and the kinetic energy. This allows the energy spectrum (and whence the depth profile) of each element in

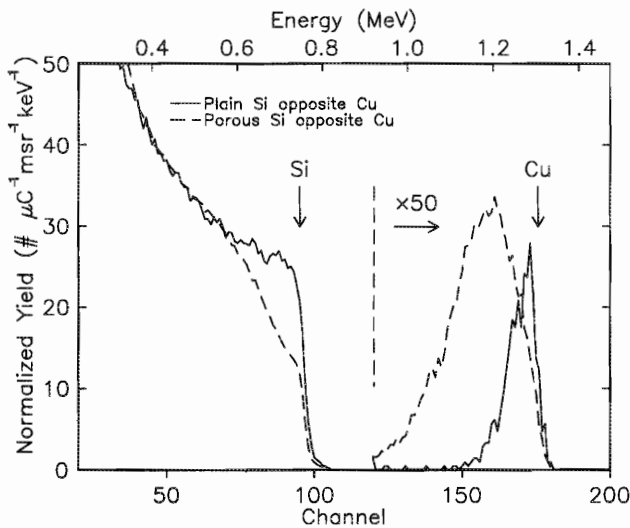
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Fig. 1. RBS spectra of the backside of a Si wafer opposite Cu deposited on the front side, and after thermal anneal treatment. Solid-line curve: clean Si surface adjacent to porous Si area; broken-line curve: porous Si area. The arrows indicate surface channels for Si and Cu. In the channel range 120–200, the spectra have been multiplied by 50 for clarity.



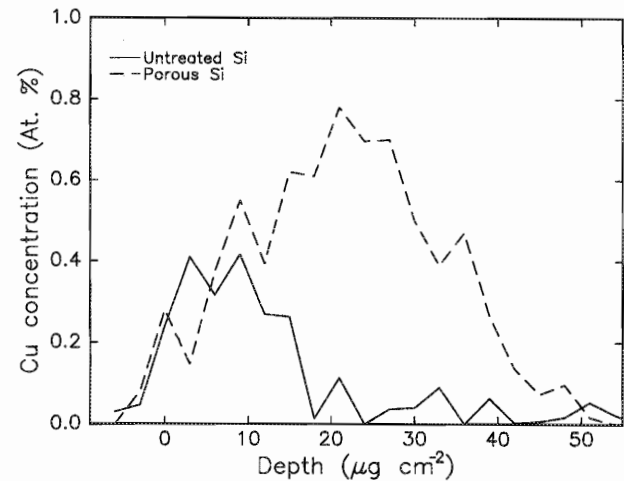
the target to be established separately. RBS yields one energy spectrum that reflects the depth distribution of all elements in the target, and which can therefore be ambiguous.

Results and discussion

Figure 1 shows two RBS spectra, taken on the backside of a sample which had a layer of Cu deposited on the front side and which had been annealed at 600 and 900°C. The broken curve was measured on a region with porous Si and the solid curve on the free Si surface adjacent to the porous Si area. The arrows indicate the channel numbers corresponding to surface scattering from Si and Cu. The content of channels with channel numbers greater than 120 have been multiplied by 50. Two differences are immediately obvious. First, both spectra show a peak in the channel range 120–180, but the peak for the porous Si sample is much larger than the other one. These peaks correspond to backscattering from Cu trapped at or near the backside of the wafer. Second, the portion of the spectrum corresponding to backscattering from Si in the near-surface area (channel range 80–100) is somewhat reduced for the porous Si sample relative to the free Si surface. The reduction in Si counts in the near-surface layer of the porous Si sample is not surprising. It is known that porous Si contains oxygen, carbon, fluorine, and hydrogen, and because of the presence of these impurities, the near-surface Si yield will be reduced. It could be pointed out that the reduction in Si signal for porous Si is not due to the porosity itself because the vacuum in the pores does not contribute to the stopping of the ions.

The Cu peaks in Fig. 1 differ in two ways. The intensity of the Cu peak on porous Si is about a factor of 3 larger than the one on clean Si. (The integrated areas under the peaks correspond to 0.77×10^{16} Cu cm⁻² for porous Si and 0.23×10^{16} Cu cm⁻² for the free Si surface, respectively.) A second difference is the position of the Cu peak. For the porous Si sample, the peak is shifted to lower energies. This is consistent with Cu

Fig. 2. Projection on the energy axis of the Cu recoil spectra, measured by ERD–TOF. Same sample as shown in Fig. 1. Solid-line curve: clean Si surface next to porous Si area; broken-line curve: porous Si area.



being trapped at the internal surface of porous Si, which is distributed over a 100 nm layer below the original Si surface. In view of these differences, the RBS results shown in Fig. 1 are consistent with getting of Cu in the porous Si layer, and that up to 0.8×10^{16} Cu cm⁻² can be gettered.

However, RBS spectra are not unambiguous. The shift in position of the Cu peak could also mean that the porous Si contains a surface impurity with an atomic number between those of Si and Cu, e.g., Cl. Because of the history of the sample, it is unlikely that anything but Cu causes the peaks in Fig. 1. Nevertheless, we have made sure that the peaks are indeed due to Cu, using ERD–TOF. The result is shown in Fig. 2. The sample used here is the same as the one giving rise to the large, shifted Cu peak in Fig. 1. In Fig. 2, only the part of the spectrum corresponding to Cu recoils is shown, projected on the energy axis. The energy channel number has been converted to a depth scale assuming a pure Si matrix. (Note that the depth scale runs from left to right whereas in Fig. 1 it runs from right to left.) The yield has been normalized by the Si yield and weighted by the ratio of the cross section for Cu and Si recoil events, which gives the Cu concentration directly. It can be seen that both surfaces gettered Cu and that again the total amount gettered in porous Si is about three times that on a clean Si surface. In addition, the Cu profile in porous Si is shifted inwards, confirming the RBS results shown in Fig. 1. Our ERD–TOF analysis also confirmed the presence of oxygen, carbon, nitrogen, and hydrogen in the porous Si layer.

The results shown in Figs. 1 and 2 show clearly that porous Si can act as a getter for Cu. We also established that the amount gettered is much less if the porous Si is opposite a part of the wafer without Cu. This shows that the Cu diffused through the wafer, as might be expected for such a rapid diffusing impurity [12]. The accumulation of Cu at the large surface area of the porous Si occurs in spite of the presence of oxygen, carbon, nitrogen, and hydrogen in the same area. This shows that an atomically pure surface, as found in microvoids, is not an absolute requirement for successful gettering. It may mean, however, that in our case the Cu is trapped not at the surface, but at the interface between Si and SiO_x. As a final

point, it is noted that the layer of porous Si can easily be removed completely by soaking in HF. This would at the same time completely separate the Cu contamination from the Si wafer.

Conclusions

A new, extrinsic sink for the gettering of Cu in Si has been found, namely porous Si. It has been shown that a layer of 100 nm of porous Si, prepared on the backside of a Si wafer, acts as a sink for Cu. A 100 nm thick layer of Cu_3Si on the front surface of the same wafer is largely dissolved when it is subjected to a 2 h long, 900°C vacuum anneal treatment. Up to $0.8 \times 10^{-16} \text{ Cu cm}^{-2}$ is found back in the porous Si, presumably bound at the large surface of the porous structure, in spite of the fact that the surface already contains large amounts of oxygen, carbon, and hydrogen.

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