Enhancement of oxidation resistance in Cu and Cu(Al) thin layers

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Abstract

High conductivity and good resistance to electromigration makes copper a promising interconnect material in microelectronics. However, one of its disadvantages is the poor corrosion resistance. Two methods of passivation are investigated and compared: Al alloying and BF²⁺ ion implantation. X-ray diffraction (XRD) and Rutherford Back-scattering Spectrometry (RBS) show the oxidation inhibition of both methods, but the different ratio of CuO₂ to CuO phases suggests different mechanisms of passivation. There are no definite oxide lines in the XRD spectrum of the implanted and annealed Cu(Al) sample, so the presence of Al and the implantation together give increased protection against oxidation. The difference between the two mechanisms of oxidation inhibition is discussed briefly. © 1999 Published by Elsevier Science B.V. All rights reserved.

PACS: 68.55.L; 61.10.N; 61.85; 81.65.M
Keywords: Copper; Aluminum; Ion-implantation; Oxidation; XRD; BS

1. Introduction

Low resistivity has made copper a widely used connect and contact material in electronics. Especially, Cu is being developed as a material of ULSI metallization due to its good electromigration resistance. However, a potential problem is that unlike the aluminum oxide the copper oxide layer is not self-protective, so the copper is readily oxidised even at low temperature. Therefore, the study of copper oxidation and the development of methods to prevent oxidation of copper surfaces have become a matter of increasing interest in the last ten years.

Different ways of protecting Cu surfaces from oxidation are discussed in the literature and involve either a protection layer [1], alloying [1–3] or ion implantation [4–9].

The present work was undertaken (i) to determine if BF²⁺ ion implantation is an effective method of copper surface passivation, (ii) to compare the passivation efficiency of Al alloying
and ion implantation and (iii) to make an effort to understand the mechanisms of passivation. The use of BF$_2^+$ ion implantation for copper surface passivation has not been reported yet in the literature to our knowledge. The advantages of using BF$_2^+$ ions compared to that of B$^+$ are the larger achievable ion current and the larger mass which leads to a shallower implanted region in case of the same energy.

2. Experimental

Cu and Cu(Al) layers were evaporated onto thermally grown SiO$_2$ layer on Si(10 0) substrates. The evaporation was performed at 10$^{-4}$ Pa pressure with resistance heating. Cu and Al were deposited from the same source to form an alloy with 8% Al composition. The composition of the source material was Cu$_{98}$Al$_2$.

Parts of the samples were implanted with BF$_2^+$ ions (40 keV energy, fluence: 9.4$\times$10$^{15}$ ion/cm$^2$). The thickness of the layers was 400 nm. The samples were oxidised for 1 h at 250°C in streaming O$_2$. X-ray diffraction (XRD) and Rutherford Backscattering Spectrometry (RBS) were used to investigate the samples before and after oxidation.

The BS spectra were recorded using $^4$He beam with an energy of 3.5 MeV at 165° scattering angle. To increase the apparent thickness of thin surface layers the samples were tilted by 60°. For separation of the corresponding peaks of Cu, Al and Si we have chosen the tilt angle to 60° and the incident energy to 3.5 MeV. The small resonance in the cross-section of oxygen situated around 3.38 MeV energy could help to determine better the oxygen amount in the deeper regions in the sample. The spectra were simulated by RBX program [10] taking into account the non-Rutherford cross-section for oxygen.

The measurements were performed in a scattering chamber under 10$^{-4}$ Pa vacuum. A liquid nitrogen cooled trap was used to avoid the carbon build up during the experiment. The beam current was typically 10 nA monitored by transmission Faraday cup [11], the collected charge was 10 $\mu$C.

3. Results and discussion

Figs. 1 and 2 show the XRD spectra of the samples before and after annealing, respectively. Before annealing only the XRD lines of the common cubic copper phase appeared. Their small shift towards the smaller angles and a line broadening shows the presence of the dissolved aluminum in the copper. (The wide peak of all the XRD spectra labeled by S in Figs. 1 and 2 at about 20 = 34° with an FWHM of about 2° arises from the (100)-oriented Si substrate. This can be observed on pure (100)-oriented Si wafers, too, and it does not change significantly due to implantation or annealing, so it is irrelevant to the discussed problem.) After annealing the lines of the Cu$_2$O and the CuO occurred and the intensity of the Cu lines decreased. However, this decrease is significantly smaller in case of the Cu(Al) samples. In the case of the implanted Cu sample, the ratio of peak intensity for the CuO lines to Cu$_2$O lines is smaller than in the un-implanted Cu sample showing a lower oxidation level for the implanted sample. In the un-implanted Cu(Al) sample, the ratio of the CuO and the Cu$_2$O lines is similar to that of the un-implanted Cu sample, but the size of the Cu lines is larger for the un-implanted Cu(Al). So the Al content inhibits the oxidation of the Cu. There are no definite oxide lines in the XRD spectra.
spectrum of the implanted and annealed Cu(Al) sample, so the presence of Al and the implantation together give increased protection against oxidation.

Fig. 3 shows the BS curves for un-implanted and implanted Cu(Al) samples, (a) as prepared and annealed and (b) as-implanted and annealed samples. In the case of pure copper layers there is no visible difference in oxygen content between un-implanted and implanted annealed samples. After annealing the very surface layers contain more oxygen. The oxygen distribution is similar to that of the un-implanted Cu(Al) sample.

It is clearly seen in Fig. 3 that the whole un-implanted Cu(Al) layer is oxidised. From the shape of corresponding Cu and O peaks we may conclude that the oxygen amount at the surface is higher. The layer has become rough and porous during oxidation as it was reported in Ref. [5]. The Cu peak shape reveals this structural change of the layer.

The implanted Cu(Al) film contains much less oxygen than the un-implanted sample. The surface of this sample is more oxidised. The internal Cu(Al)/SiO₂ interface remained abrupt which also indicates only slight oxidation of the layer.

The RBS investigations confirm the passivation efficiency of Al alloying and implantation. The amount of the oxygen was found to be the smallest in case of the implanted Cu(Al) sample. A remarkable difference between the oxygen distributions is that under a highly oxidised surface layer the oxidation rate is much smaller in the case of implanted Cu(Al).

The oxidation mechanism of the pure copper has been properly studied [12–14]. A thin layer of Cu₂O forms first on the copper surface. The Cu₂O is a p-type semiconductor with negatively charged vacancies. The growth of the oxide takes place on the top surface: the Cu⁺ ions transport through the oxide via vacancies. In case of polycrystalline copper films the role of the grain boundaries is also
important [5]. The oxide film is usually stressed or porous, because the molar volume of the Cu$_2$O phase is much higher than that of the copper. The second stage of oxidation, the formation of the oxygen rich CuO from Cu$_2$O is usually a slower process at lower temperatures. It is governed by the in-diffusion of oxygen into the oxide. This becomes dominant if the Cu$^+$ transport in the Cu$_2$O phase is inhibited by an implanted or alloyed impurity, and the mass ratio of CuO to Cu$_2$O is larger than in case of oxidation of pure Cu. Ding et al. found a reduced oxidation rate and the formation of CuO rather than Cu$_2$O on the surface in all the three cases of Al$^+$ and B$^+$ implantation and aluminum alloying [2]. They believe the mechanism for this reduced oxidation rate is the same: the impurities occupying the vacancy sites inhibit the transport of the Cu$^+$ ions in the oxide. The same mechanism can be assumed in case of our Al-alloyed Cu sample: relatively strong Cu and CuO XRD lines are present together. However, in case of the BF$_2^-$ implantation the appearance of the strong Cu$_2$O lines and weak CuO lines shows that the mechanism of oxidation is similar to that of the pure Cu, but in this case it is retarded. We suppose that this retardation is caused by the restricted penetration of oxygen to the layer. This can be a consequence of a protection layer induced by the shallow implantation or a new, B or F containing compound passivating the grain boundaries. A protection layer can explain the difference in the oxygen distribution of the un-implanted and implanted Cu(Al) layers, i.e. the highly oxidised bottom layer in the un-implanted and the lack of it in the implanted sample. The enhanced oxidation protection in the implanted Cu(Al) sample is due to the common effect of these two different mechanisms.

4. Conclusion

Two methods of copper surface passivation: Al alloying and BF$_2^-$ ion implantation were investigated and compared. X-ray diffraction and BS showed the oxidation inhibition of both methods but the mechanisms of passivation seem to be different. In case of Al alloying the outdiffusion of Cu$^+$ ions is probably inhibited, in the implanted samples the penetration of oxygen is supposed to be blocked. The presence of Al and the implantation together give increased protection against oxidation.

Acknowledgements

This work was partially supported by the Hungarian Scientific Research Fund (OTKA) under project numbers T023705, T016667, T025928 and T016506.

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