Influence of Cu diffusion conditions on the switching of Cu–SiO$_2$-based resistive memory devices

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ABSTRACT

This paper presents a study of Cu diffusion at various temperatures in thin SiO$_2$ films and the influence of diffusion conditions on the switching of Programmable Metallization Cell (PMC) devices formed from such Cu-doped films. Film composition and diffusion products were analyzed using secondary ion mass spectroscopy, Rutherford backscattering spectrometry, X-ray diffraction and Raman spectroscopy methods. We found a strong dependence of the diffused Cu concentration, which varied between 0.8 at.% and 10$^{-3}$ at. %, on the annealing temperature. X-ray diffraction and Raman studies revealed that Cu does not react with the SiO$_2$ network and remains in elemental form after diffusion for the annealing conditions used. PMC resistive memory cells were fabricated with such Cu-diffused SiO$_2$ films and device performance, including the stability of the switching voltage, is discussed in the context of the material characteristics.

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1. Introduction

There is currently a tremendous drive to develop non-volatile devices which will ultimately replace Flash memory. The requirements demanded of such replacements include high operating speed, non-destructive reading, low energy programming, compatibility with the complementary metal–oxide–semiconductor (CMOS) process, and low fabrication costs. One very promising solution involves switching based on devices in which solid electrolytes combined with one oxidizable and one inert electrode constitute the active structure. This is the basis of Programmable Metallization Cell (PMC) memory devices. These utilize the reduction of nanoscale quantities of metal ions in the solid electrolyte film to form a metal link between the two electrodes and thereby switch the device from a high resistance to a low resistance state. Due to the electrochemical nature of the process the metal link can be dissolved by application of opposite bias on the electrodes so that the device can be returned to its high resistance state. Devices based on Ge-chalcogenides combined with Ag or Cu, and WO$_3$ combined with Cu gave promising results in the context of PMC resistance change devices [1–3]. The specific benefits of these devices come from their widely spaced resistance states, low programming voltage/current, possibility for multilevel storage, and high scaling capability. One very important characteristic of these devices is that the memory is non-volatile due to the fact that the data-representing resistance change is caused by the formation of a feature formed from neutral atoms, which do not, of course, display the same leakage-based retention failure mechanisms of charge-based memories. The application of SiO$_2$ in the active medium of PMC memory elements proved to be a viable alternative to chalcogenide- or transition oxide-based materials [4]. The main advantage of SiO$_2$-based devices is their ease of integration in CMOS technology, particularly in the back-end-of-line sequence, where the fabrication processes necessary for the device formation are already in use. The initial findings from the characterization of such devices have shown promising results [5]. However, for this material to reach its full potential in this application, the materials must be fully characterized.

There are two intrinsically related aspects of equal importance which need to be addressed in order to achieve performance optimization of SiO$_2$-based PMC devices; one is to identify which composition gives the best device performance and the other is to determine what processing is necessary in order to produce devices with specific parameters. Critical to this enhanced understanding is a determination of how the Cu interacts with the SiO$_2$ network, what the distribution of Cu within the SiO$_2$ film is, and what is the new structure forming after Cu is embedded in the film. SiO$_2$ has been used as both a dielectric and a barrier in the semiconductor industry for decades and so the diffusion of metals in this material is well understood. From these studies, it is known that Cu has a higher diffusivity in SiO$_2$ than other metals such as Fe [6], however, Cu solubility in SiO$_2$ films is still expected to be quite limited. This opens up some challenges for the characterization methods due to the expected low concentration of Cu in the hosting oxide film.
In our previous work we noted that the introduction of Cu by photodiffusion (as used in the formation of Ge-chalcogenide solid electrolytes) is not favored [4] due to the specific bond organization and strength of the chemical bonding in SiO₂. Other options are thermal diffusion and ion implantation which have been successfully applied to the introduction of Cu in SiO₂ films [6,7]. We have used thermal diffusion since this method of metal introduction is more acceptable than Cu ion implantation in mainstream semiconductor processing due to the lack of readily available implant sources. In this article we discuss the results of Cu diffusion into SiO₂ films at different annealing temperatures and times. Data is presented regarding the new structure forming after Cu diffusion in the hosting SiO₂ film and its depth distribution using a variety of characterization techniques. These material characterization results are related to the performance of PMC devices prepared under different conditions.

This work is aimed at giving a general perspective of the material options that could be used in device fabrication and to be a model for the explanation of device performance as a function of processing conditions.

2. Experimental details

2.1. Material stack preparation

All material characterization experiments were performed on blanket films of Cu-doped SiO₂ on a TiN/Si substrate. The TiN layer formed a diffusion barrier for Cu and prevented Cu diffusion into the Si substrate. In this manner we avoided the opportunity for contact between the diffused Cu and the pure Si substrate, which could lead to additional reactions that would complicate the interpretation of the experimental results. The SiO₂ and Cu films were deposited using a Torrvac VC-320 electron beam evaporator at an average evaporation pressure of 4 × 10⁻⁴ Pa and 0.2 nm/s deposition rate. The stack sequence for the material characterization samples from top to bottom was as follows: 750 nm SiO₂; 350 nm Cu; 550 nm SiO₂; 80 nm TiN. The top SiO₂ layer was used to prevent the oxidation of the Cu film during the thermal processing of the samples. The high temperature thermal doping of SiO₂ with Cu was carried out in a Lindberg Tube Furnace in an N₂ (flowing) ambient. The stacks were split into several groups, each one annealed at 560 °C, 660 °C, or 720 °C for 15 min, 1 h or 2 h respectively. After high temperature processing, the top SiO₂ layer was used to prevent its oxidation during the thermal treatment. This layer was etched off using another lithography and etch process. 15 nm of SiO₂ and 40 nm of Cu were deposited on the patterned substrate under similar deposition conditions as the samples used for material characterization. The top electrode (Cu) for electrical probing was then patterned by a lift-off process. A protective layer of SiO₂ was deposited on top of the Cu electrode to prevent its oxidation during the thermal treatment. This layer was etched off using 20:1 BOE after the annealing process. The annealing conditions of the devices were at 560 °C, 660 °C and 720 °C for 15 min in N₂ (flowing) ambient.

2.2. Device preparation

A schematic of a typical PMC device structure is shown in Fig. 2. A 100 nm thick tungsten layer was deposited using a chemical vapor deposition (CVD) process on thermally grown SiO₂ on a Si substrate. 100 nm of silicon nitride was deposited on top of this tungsten layer using CVD and vias which define the active device regions were patterned using optical lithography and etched using a reactive-ion etching process to expose the bottom tungsten film. The via diameters varied from 5 μm to 0.18 μm. Probe windows to contact the tungsten bottom electrode were opened up using another lithography and etch process. 15 nm of SiO₂ and 40 nm of Cu were deposited on this patterned substrate under similar deposition conditions as the samples used for material characterization. The top electrode (Cu) for electrical probing was then patterned by a lift-off process. A protective layer of SiO₂ was deposited on top of the Cu electrode to prevent its oxidation during the thermal treatment. This layer was etched off using 20:1 BOE after the annealing process. The annealing conditions of the devices were at 560 °C, 660 °C and 720 °C for 15 min in N₂ (flowing) ambient.

2.3. Material characterization

X-ray diffraction analysis (XRD) was used to identify phases formed in the as-deposited and annealed samples. One degree glancing scan XRD was performed using a Phillips X’pert MPD diffractometer. Cu Kα radiation was used as the source and samples were investigated over an angle range of 5°–100° with 0.01° step size and 1 s per step. The voltage and current settings were 45 kV and 40 mA respectively. In the glancing scan XRD analysis, the angle of source from the sample surface is fixed at a lower value (1° in our case) while the detector moves in the usual manner. In a 0°–2θ geometry scan, the angle of incidence is always equal to the angle of exit. Hence, at higher angles to detect higher plane reflections, the penetration depth of X-rays may be greater than the thickness of a thin film, resulting in unwanted substrate peaks and noise. Glancing angle X-ray diffraction reduces this to a significant extent, however, it provides a larger interaction volume within the studied thin film as compared to the 0°–2θ geometry scan.

Rutherford backscattering spectrometry (RBS) was performed using a 2.0 MeV He⁺ ion beam at a tilt of 8° in a General Ionex Tandetron accelerator. A tilt of 50° was used as well to improve depth resolution and verify the Cu distribution in the film. A computer program RUMP was used to simulate RBS spectra [8].

Secondary ion mass spectrometry (SIMS) was done in a Cameca IMS 3f magnetic-sector SIMS instrument. O²⁻ ions at 17 keV and 50 nA ion current were used as the primary ions since their application minimizes the charging problems in the SiO₂ films. Positive ion mass spectra and depth profile were obtained. The depth scale of the depth profile was determined from Tencor stylus profilometer linescan measurements across the sputter crater.

Raman spectra were recorded using a Raman spectroscopic system, Horiba Jobin Yvon T64000, in backscattering geometry. The 441.6 nm laser line of the helium–cadmium continuous wave laser...
(Kimmon Koha Co., Ltd. IK5752 I-G) at a power of 83 mW was used for the excitation at an acquisition time of 1 min. The signal was analyzed with a thermoelectrically cooled CCD camera.

2.4. Device characterization

The switching characteristics of the devices annealed at different temperatures were studied using slow voltage sweeps. These were applied by connecting the device electrodes via tungsten probes held in a micromanipulator in a probe station to a semiconductor parameter analyzer (Agilent 4155C). Voltage double sweeps were used, starting at $-0.75\,\text{V}$ (copper electrode negative and tungsten electrode positive), sweeping to $1.5\,\text{V}$ (copper electrode positive and tungsten electrode negative), and sweeping back again to $-0.75\,\text{V}$. For a typical PMC device with oxidizable and inert electrodes, this double sweep should have put the devices in an erased (high resistance) state to start with, written them with the positive bias, and then erased them with the final negative bias, however, as we will see later, some devices in this study showed unipolar (the same polarity for both write and erase) characteristics. The compliance current setting in the 4155C was used to limit the current passing through the device once the device was written.

3. Results

The results regarding the amount of copper diffused into the SiO$_2$ films measured by SIMS are shown in Fig. 3. Concentration is calculated with respect to silicon by assuming that the ion yield of Cu$^+$ and heavily oxidized silicon is approximately the same (within a factor of 5). The ratio of Cu$^+$/Si$^+$ is then taken as the concentration of Cu$^+$. The interface profile is not characterized by a sharp difference between the two films which is an indication that the interdiffusion starts even during the time of the copper film deposition. There is approximately three orders of magnitude difference in the amount of diffused Cu for the two temperatures studied; approximately 0.8 at.% for diffusion at 720 °C and around $10^{-3}\,\text{at.}%$ for diffusion at 560 °C. The spectra follows the standard Cu$^{63}$ and Cu$^{65}$ isotope ratio nicely.

Fig. 4a) and b) shows the RBS spectra taken from a Cu-doped-SiO$_2$/TiN structure. The amount of Cu diffused in the SiO$_2$ film after annealing at 560 °C could not be detected in this experiment since it is below the sensitivity limit of the technique. For the sample annealed at 720 °C for 15 min the experimental curve shows a faint signal near channel 300 in addition to the major Si and oxygen peaks. Ti also produces peaks close to this region. Furthermore, we see two more peaks close to channel 400. Since the signals from Cu and Ti are very close, fine calibration is needed for a detailed description of the composition studied. We suggest that the signal at channel 300 comes from Ti under the SiO$_2$ film, and the wide signal at channel 320 belongs to Cu at the SiO$_2$/TiN interface. Given that the width of the Cu peak is greater than the system energy resolution (~7 channels), this is an indication that Cu exists at the interface with the TiN. The signal at channel 430 reveals a surface nature and we assign it to the Cu that is part of the first diffused quantity.

Fig. 5 shows the XRD data collected from our films. Among the numerous peaks that are characteristic for all the participating elements and compositions we can observe those of Cu which are the only peaks...
related to this element, i.e., our results show that Cu remains in elemental form during processing. The intensity of these peaks rises with increasing annealing temperature.

The Raman results in Fig. 6a) and b) show in a most impressive manner the dependence on the film’s characteristic upon the annealing conditions. The Raman mode intensity characteristic for the SiO$_2$ films decreases with increasing annealing time or temperature and no new features occur with the extension of the annealing conditions. Note specifically the strong decrease of the Raman activity with temperature caused by annealing at 660 °C. The films are characterized by a relatively sharp band at 440 which arises from symmetrical Si–O–Si stretching modes principally involving motion of the oxygen atom. The modes at 510 and 640 cm$^{-1}$ occur from symmetric stretching modes of small-ring configurations in the three-dimensional random network [9]. There are two very weak features at 1060 and 1190 cm$^{-1}$ which are not shown because of their low relevance and for a clearer presentation of the modes at lower wavelengths.

Note that Cu is not expected to appear on these spectra since it is Raman silent [10] but its presence in the films can be inferred from the reducing Raman activity of the hosting film due to its increased conductivity because of the Cu inclusion. If Cu oxidation occurred during the annealing process, features could be expected in the 290–624 cm$^{-1}$ region [11].

Fig. 7a) and b) shows representative I–V characteristics of devices formed by films annealed at 720 °C and 660 °C, respectively. Note that both unipolar and bipolar switchings are possible. The progression of the voltage sweep is shown with the help of numbered arrows, indicating the direction of the voltage sweep and the sequence of the events during the sweep. The device conducts a current equal to the compliance current, 25 µA in this case, when it is written or switched ON at the switching threshold voltage. The device conducts negligible current once it is erased or switched OFF. In Fig. 7 a), which shows symmetrical unipolar switching (both write and erase in either polarity), the device follows a sequence of OFF(4)–ON(5)–OFF(9)–ON(12), (the numbers in parentheses refer to the corresponding numbered arrow in the figure). In the case of the bipolar switching shown in Fig. 7 b) it follows the sequence ON(3)–OFF(8). In both cases, three consecutive voltage sweeps are shown. It should be noted that the switching threshold is higher (~0.5 V) for the bipolar switching device. The switching threshold shows a close dependence on the annealing temperature and decreases for samples with films annealed
of films with increased porosity. It is for this reason, and the others given above, that the Cu diffusion is significantly accelerated at higher temperature. We see evidence for this increased diffusivity in the Raman spectra where at increased annealing time and temperature the intensity of the Raman modes decreases due to the higher conductivity of the material with higher metal concentration.

Next, we have to consider the fact that we are dealing with a multilayer structure which can result in significant thermal stress and residual strain-induced effects. For example, it has been noted that the void formation rate in SiO₂ with a Cu metal film deposited on top increases with an increase in temperature [16]. In general, due to the difference in the thermal expansion coefficients of the different films in the stack, significant stresses are expected to occur in the hosting medium. Indeed, the slight shift of the Raman modes compared to the relaxed SiO₂ [9] is an indication of the strain occurring in the material. Stress- or point-defect relaxation can occur at any of the studied temperatures and this is an additional reason for enhancement of the diffusion process. Pan et al. [7] noted an optimum annealing condition around 600 °C to improve indentation induced precipitation. Our results show a drastic decrease in the intensity of the Raman breathing modes after annealing at 660 °C which is an indication for enhanced Cu diffusion at this temperature. The same Cu-related trend is noted for the threshold voltage for the first sweep which is considerably lower in the devices annealed at 660 °C compared to those annealed at 560 °C. Our assumption is that the latter devices have higher switching thresholds due to the lower concentration of Cu introduced into the SiO₂ matrix, while for those annealed at 660 °C there is well expressed nanoparticle precipitation and growth [7] which contribute to the devices switching at lower threshold voltage.

From the XRD results, we conclude that Cu does not react with the constituents of the SiO₂ network and remains in elemental form when diffused into the dielectric film, leaving most Si atoms in a configuration with four oxygen bridging atoms. The lack of formation of CuO or other oxides, silicates or silicides was also demonstrated by our Raman spectra. Our results are in a good agreement with the data reported by Dallaporta et al. [16]. Moreover the Cu transport that we will discuss next is also suggestive that Cu remains free into the SiO₂ matrix. These results contradict the data described by Cao et al. [17] who suggest the formation of Cu₃Si in their study of the diffusion processes in the Cu/SiO₂/Si system at temperatures over 450 °C. We believe that their result is a consequence of the fact that Cu, due to its relatively high diffusivity, has reached the SiO₂/Si interface as discussed earlier and formation of silicides is possibly due to Cu reaction with pure Si.

Applying our newly-gained knowledge of material characteristics to the electrical performance of the PMC devices studied, we can better comprehend their operation. Since the concentration of Cu is quite low in the as-diffused glass in all cases, there will be insufficient metal to significantly influence the resistivity of the material and hence the resistance of the device will be relatively high. When a positive bias is applied across the Cu-doped films via a Cu electrode, which can be regarded as a supplier of Cu⁺, accelerated diffusion of Cu⁺ will occur due to the reduction in the activation energy [18,19] and the presence of the large number of voids and pathways in the host glass, as discussed above. One can conclude that resistance reduction in the devices is due to the addition of Cu into the void-filled random network of the hosting glass, where it joins the existing Cu to form conducting Cu-rich pathways. An opposite bias (Cu electrode negative) takes this added material out of the glass and back to the Cu electrode by the same process, returning the device to its high resistance state.

As noted above, annealing at higher temperatures results in much more Cu being introduced into the SiO₂ due to the larger number of voids formed compared to the lower temperature annealing cases. It is likely that this same void-rich structure will also allow Cu to enter the film more easily under positive bias. We suggest this is the reason that devices formed from material diffused at higher annealing temperature

![Fig. 9. Switching threshold variation with subsequent voltage sweeps.](image)

at higher temperature as shown in Fig. 8. We show the threshold voltage occurring after the first sweep since it gives a better understanding of the influence of the thermal doping alone, because switching in the subsequent sweeps could be influenced by a change in the material caused by the previous voltage sweep. Indeed, multiple sweeps show that switching on average occurs at lower threshold voltage after the initial sweep, particularly for the lowest annealing temperature, as shown in Fig. 9.

4. Discussion

We will start our discussion with some remarks about the host SiO₂. Although this material has been widely studied, there is little data regarding SiO₂ films formed by e-beam evaporation, which could be due to the fact that this method of film formation is not typically used in conventional Si processing. The films are amorphous as revealed by the wide Raman and XRD features. In our case, the e-beam evaporated film was deposited over a polycrystalline TiN film. Hence, one can expect an increased number of defects compared to a thermal oxide grown on single crystalline Si. Indeed the appearance of the ‘defect Raman bands’ at 510 and 640 cm⁻¹ on Fig. 6 a) and b) is direct evidence of the high disorder of the structure [9]. This disorder will result in the formation of voids within the oxide film which are favorable for the diffusion process and almost certainly play a role in the switching process (discussed later). Note that although the structure of our evaporated oxide differs from that of thermally grown oxide, it will be close to that of sputtered oxide, particularly with the slow deposition rate used. We can infer this from PMC device characteristics, which are quite similar for evaporated and sputtered oxides.

Cu has a relatively high diffusivity in SiO₂ and isotope tracking analysis shows that it can penetrate far into an SiO₂ film [12,13]. Moreover, this latter study has shown that Cu can move bidirectionally (in and out of the oxide film) which is an indication that it does not chemically react with the SiO₂ matrix. This result is in a good agreement with the RBS data obtained in our study where we identified Cu at the SiO₂/TiN interface as well as near the Cu/SiO₂ surface, which is also a sign of the high mobility of Cu in the SiO₂ film. A similar distribution has also been reported by Sun et al. [14].

When we discuss the thermal diffusion of Cu into the SiO₂ film, we have to consider the temperature-related changes occurring within the hosting material. It has been found that by increasing the temperature, electronically excited states are accumulated in the skeletal Si−O bond system as well as by formation of associates in the cationic and anionic sublattices [15]. The net result of this is that an additional energy reservoir appears which is favorable for the diffusion process at increased temperatures. Moreover, the dynamic exchanges in the structure of the hosting SiO₂ film leads to formation
have a lower threshold voltage. This chemically stable but “open” structure facilitates the transport of Cu and at the same time does not create conditions for the chemical stabilization of Cu as oxide within the glass. We also believe that the fact that Cu does not form chemical bonds with the SiO₂ host is the reason for the fluctuations in the threshold voltage values from device to device obtained for the same programming conditions (see Fig. 8) and during multiple sweeps (Fig. 9), as the unbound Cu can readily be thermally (during processing) or electrically (during programming) redistributed within the film. Note also that the multiple sweeps result in minimum threshold dispersion at an annealing temperature of 660 °C (Fig. 8) and we therefore believe this is close to the optimal conditions for solid electrolyte formation. The decrease in the average switching threshold voltage with consecutive sweeps, particularly evident in the case of the samples annealed at 560 °C which have the lowest initial (as-processed) Cu content and show a 0.1 V average drop after five sweeps, could very well be indicative of a type of “conditioning effect”. Such a large drop in threshold voltage is not seen in the samples which have been annealed at the highest temperature and therefore have the highest as-processed Cu content. We believe that the electrical condition which leads to the drop in threshold voltage is due to the net addition of Cu during cycling (fewer Cu ions are removed from the SiO₂ during the erase than are introduced during the write), so that the Cu concentration is brought closer to an equilibrium level with increasing sweep number. The samples annealed at higher temperature are already closer to this equilibrium level following processing and therefore do not exhibit such a strong threshold reduction effect.

The appearance of devices processed at higher temperature which exhibit both symmetrical unipolar and non-symmetrical bipolar switchings can be understood by considering the RBS results (Fig. 4b). We believe that this effect is related to the fact that in some instances, Cu diffuses across the entire thickness of the SiO₂ film to the SiO₂/W interface, thus forming a symmetrical Cu–SiO₂–Cu structure which leads to programming or erasing in either direction. Note that in such devices, the erase mechanism could involve the thermal dissolution of the conducting Cu filaments due to Joule heating, rather than an electrochemical oxidation of the metal. In the case of bipolar switching, Cu remains in the SiO₂ volume and the devices only program and erase under Cu electrode positive and Cu electrode negative biases respectively, as expected for non-symmetrical device structures.

5. Conclusions

In this work we present material characterization of Cu-doped SiO₂ films which are used as the active film in PMT resistive switching devices, and link the material properties to switching characteristics. It was found that for the range of annealing conditions used (560 °C to 720 °C), the thermal diffusion product for Cu films on evaporated SiO₂ layers is an oxide matrix with embedded unreacted Cu atoms. This result has been confirmed by XRD and Raman measurements. Based on the characterization data, we propose that Cu diffusion in SiO₂ occurs via channels and voids formed in the glassy network, the presence of which increases with an increase in the annealing temperature and results in high Cu concentration within the film. The electrical characterization of PMT devices formed from these materials shows a close relationship between the threshold voltage of the devices and the annealing conditions for Cu diffusion. The lowest threshold voltage was obtained for material diffused at the highest temperature because of the high Cu concentration due to the higher number of voids present at this temperature. The fact that Cu does not form chemical bonds with the SiO₂ network allows the Cu to remain mobile within the oxide which leads to variations in the switching threshold voltage from device to device following processing and fluctuations in this parameter in the same device during programming sweeps. The smallest variations are observed with films annealed at 660 °C. The average switching threshold voltage of samples annealed at the lowest temperature is found to decrease with the number of write–erase cycles. This is most likely due to the Cu ion concentration approaching an equilibrium value during cycling in these initially low Cu concentration samples as the effect is not so evident in the case of high Cu content materials produced by annealing at higher temperature. Higher temperature annealing can result in the formation of devices with a Cu/SiO₂/Cu structure as Cu could diffuse through the entire volume of SiO₂ and accumulate on the interface with the bottom electrode, forming a symmetric structure. These devices tend to show symmetric unipolar switching. Non-symmetric bipolar switching is exhibited by devices with a Cu/SiO₂/W structure, more typical of moderate to lower temperature annealed devices.

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