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Charge storage characteristics of metal-induced nanocrystalline in erbium-doped amorphous silicon films

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Abstract

Amorphous silicon film (α-Si) doped with uniform erbium (Er) impurities is deposited by laser ablation technology. High density silicon nanocrystals (nc-Si) can be formed after the rapid thermal annealing (RTA) process. The crystalline process can be explained as the "metal-induced nanocrystalline mechanism", i.e., doped erbium atoms introduce additional strain in the amorphous silicon matrix and behave as nucleation centers during the thermal annealing process. Through this method, Si nanocrystals with high density and self-limited size distribution can be obtained. The experimental results demonstrate that the Er-induced nanocrystalline silicon film has good charge storage characteristics. It is shown that the optimal condition for the Er-induced nanocrystalline layer in α-Si is with 1 wt.% Er concentration and 1100 °C RTA process for 30 s.

Keywords: Nanocrystal memory; Charging; Metal-oxide semiconductor (MOS); Metal-induced nanocrystalline

1. Introduction

With the semiconductor nonvolatile memory (NVM) stepping into the nano-scale filed, nanocrystalline silicon (nc-Si) has been put forward as the replacement for the continuous polycrystalline silicon floating gate due to the discrete charge storage and long retention time [1]. To date, various methods for preparing nc-Si have been reported, for example, chemical vapor deposition (CVD), low energy implantation of Si, and thermal anneal of silicon rich silica [2–5]. In order to obtain larger memory window, a high density silicon nanocrystals with uniform size distribution are desired. As a result, it is expected that both of the nc-Si density and the size fluctuation can be controllable during the fabrication process. One way to realize this goal is to prepare layered arranged Si nanocrystals, which can be accomplished by deposition of $SiOx/SiO_2$ multilayer followed by a high temperature annealing [6]. Moreover, the multilayer stacked nc-Si structure has also been reported to enhance the charge retention ability. The modulation of the Si nanocrystal density can be achieved through the variation of the stoichiometry parameter x of the $SiOx$ layers [7]. Another way is to thermally process a thin α-Si film or germanium film sandwiched between two SiO_2 dielectric layers by rapid thermal annealing (RTA) [8]. However, the nanocrystalline process by annealing α-Si films is uncontrollable for both the density and the size distribution. It has been reported that the doped Erbium (Er) atoms can introduce additional strains in the α-Si matrix and behave as nucleation centers during the thermal annealing crystallization [9]. The average size of the nc-Si is almost independent of the crystallization time with a certain Er concentration and annealing temperature. Through this way, nc-Si luminescent efficiency is improved, which means a higher Si nanocrystalline density was achieved.

In this study, α-Si film doped with uniform Er impurities is deposited by laser ablation technology. High density and small

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size metal-induced nc-Si is achieved by RTA. Experimental results show the metal-induced silicon nanocrystals have reasonable charge storage performances for the nonvolatile memory applications.

2. Experimental details

First, a tunnelling oxide layer (2.5 nm) is formed by dry thermal oxide process on p-type Si (110) substrate. Then the Er-doped α-Si layer with thickness of 3 nm is deposited on the tunnelling oxide by laser ablation technology. During the laser ablation deposition process [10], the initial material was a ceramic target, a mixture of Si and prescribed amount of 1 wt.% or 30 wt.% Er_2O_3. A Q-switched YAG laser ($4\omega_0$=266 nm, 1 J/cm^2) was used to ablate the target in a vacuum chamber with a background pressure of 6.6×10^{-5} Pa. The RTA processes between 700 °C and 1100 °C are carried out in N_2 atmosphere to crystallize the Er-doped α-Si films. The temperature ramp rate is about 120 °C/s. The annealing time only includes the holding period. Finally, control silicon oxide (20 nm) and aluminum electrodes are deposited and evaporated, respectively, on top of the α-Si film to form a metal-oxide–nanocrystal-oxide-silicon structure for the capacitance–voltage (C–V) measurement. The cross section transmission electron microscopy (TEM) image is analyzed by Hitachi H-9000 NAR HRTEM (with 300 kV high accelerating voltage). The C–V measurements are performed at 1 MHz using an HP 4284A analyzer at room temperature.

3. Results and discussion

As for the thin Er-doped α-Si film (denoted as ErSi film), RTA process is adopted to achieve the metal-induced nanocrystalline layer for high technical efficiency. Here, metal-oxide-silicon (MOS) capacitor structure is prepared for the C–V measurement. After RTA process, nc-Si will come into being from the former continuous α-Si film. Fig. 1 shows the cross section TEM image of the metal-induced nc-Si structure. It can be seen that the Si nanocrystals are embedded in the α-Si film. Since the thickness of α-Si film is limited in a region, the nc-Si size is also self-limited. As can be estimated from the TEM image, the prepared Si nanocrystals have a size of 2~3 nm and a high density of 2×10^{12}/cm^2.

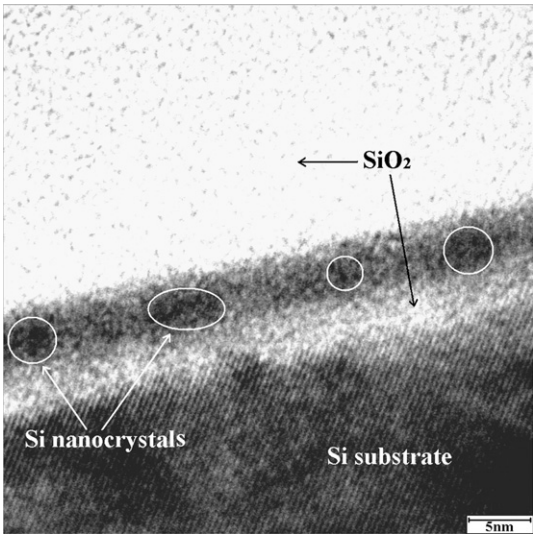

Fig. 1. Cross section TEM image of the metal-induced nc-Si structure with Si nanocrystals embedded in the ErSi film with 1 wt.% Er concentration and annealed at 1100 °C for 30 s.

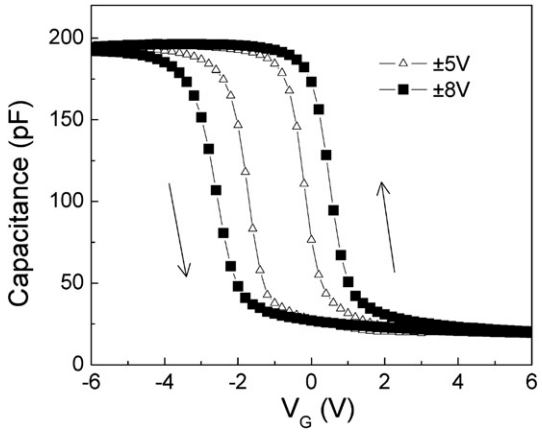

Fig. 2. C–V hysteresis under 5 V and 8 V bidirectional gate scan voltages for the sample with 1 wt.% Er concentration annealed at 1100 °C for 30 s.

The C–V measurement is performed to evaluate the memory effect of the fabricated structure. Fig. 2 shows the typical C–V curve of the 1 wt.% ErSi sample (annealed at 1100 °C for 30 s). As can be seen from the curve, the flat band voltage shift (ΔV_{FB}) can reach 3 V under ±8 V bi-direction gate scan voltage, which means metal-induced nanocrystalline in ErSi film has good charge trap characteristics.

The effect of different annealing conditions on charge trap characteristics for different Er impurity concentrations is also investigated. Pure α-Si film and ErSi film with different Er weight ratios are both studied. The curves of ΔV_{FB} versus annealing temperatures are shown in Fig. 3. The values of ΔV_{FB} are obtained under ±8 V bi-direction scan range. As can be seen in Fig. 3, when the RTA temperature is below 900 °C, ΔV_{FB} values is small for all samples, which indicates a low density nanocrystals and a poor crystallization process. This may be due

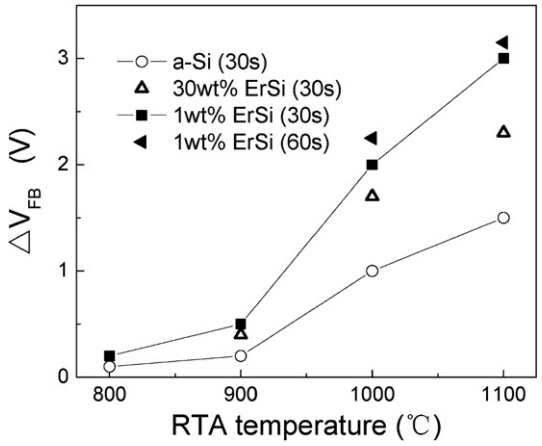

Fig. 3. Flat band voltage shift as a function of RTA temperature for samples prepared with different Er concentration and annealing time.

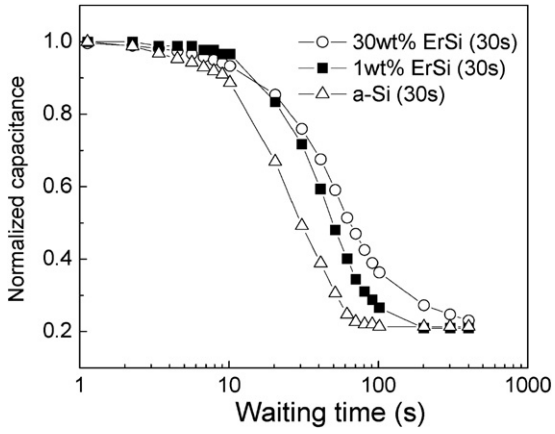

Fig. 4. Retention characteristics indicated by capacitance loss as a function of waiting time for samples prepared without and with 1 wt.% and 30 wt.% Er concentration and annealed at 1100 °C for 30 s.

to the fact that most of the α-Si films still remain amorphous at such temperature, resulting in insufficient charge trapping. This process can be obviously optimized at 1000 °C and above. It should be noted that at 1000 °C, all the ErSi samples have larger memory window than the pure α-Si film, which indicates that Er has higher crystalline efficiency in inducing the crystallization process in ErSi film. The doped Er atoms introduce additional strain in the α-Si matrix and behave as nucleation centers during the crystallization [9]. The high density Si nanocrystals induced by Er atoms enhance the charge trap ability of the thin film. As a result, it is naturally expected that the increase of Er atom concentration in the ErSi film will result in higher nc-Si density due to more nucleation centers. However, it is found in the experiment that 1 wt.% samples have larger ΔV_{FB} than the 30 wt.% samples, as can be seen in Fig. 3. One possible reason is that the overabundant Er accumulation will lead to adjacent nucleation center join together, resulting in a lower nc-Si density. The optimal Er doping level for the best charge storage characteristics should be detailed investigated in further work. Based on the experimental observations in present work, 1 wt.% Er concentration is a reasonable level.

The impact of the annealing time on charge storage characteristics is also shown in Fig. 3. For the samples with 1 wt.% Er concentration, a small ascending trend of ΔV_{FB} with the increase of annealing time is observed. However, it is noted that the effect of annealing temperature seems to be more prominent than that of the annealing time on ΔV_{FB}. According to the discussion above, the optimal condition for the Er-induced nanocrystalline layer in α-Si film is with 1 wt.% Er concentration and 1100 °C at 30 s RTA process.

The charge retention characteristics of these samples are measured to evaluate the superiority of the Er-induced nanocrystalline, as shown in Fig. 4. For the charge retention measurement, +8 V gate voltage was applied for 3 s and then the capacitance was measured at a constant DC voltage bias (−0.5 V) with an interval. The capacitance decreases with the waiting time increasing, indicating charges were gradually lost. Less change of the capacitance means better charge retention characteristics. As can be seen in Fig. 4, the discharging velocity is quite fast, indicating a poor retention behavior. This may be due to the ultrathin tunnelling oxide (2.5 nm). The overall retention performances will be better improved by utilizing a thicker tunneling oxide. The ErSi films have better retention characteristics than pure α-Si film, which can be partially attributed to the different nc-Si density in the film [11]. The better charge retention characteristics of ErSi film benefit from the high density nanocrystals. Moreover, it can be seen that 30 wt.% ErSi sample has the best retention performances. It is a hint that higher Er concentration conduces to a longer retention time. This phenomenon may be attributed to the Er atoms near the interfaces between the Si nanocrystals and around α-Si. The charges trapped in the interface of nc-Si will partially transfer into the assistant charge trap centers of the Er Silicide, which is formed in the metal-induced nanocrystalline process. The high work function [12,13] and less impact of quantum confinement effect [14]of metallic material enhanced the retention capability of the film [13,14].

4. Conclusion

Feasibility of utilizing laser ablation prepared Er-doped α-Si film (3 nm) to fabricate the silicon nanocrystals is investigated. A high density metal-induced nanocrystalline layers can be obtained after rapid thermal annealing process. The MOS structures of Al–SiO_2–ErSi–SiO_2–Si were prepared for C–V measurement. Experimental results show that a suitable Er concentration will bring with high density nanocrystalline in α-Si film. Though higher Er concentration will help to improve the retention characteristic, it will not always increase the nanocrystal density. Metal-induced nanocrystalline is an efficient way to fabricate high density and self limited size distribution Si nanocrystals for nonvolatile memory applications.

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