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Effect of the blistering of ALD Al_2O_3 films on the silicon surface in Al- Al_2O_3 -Si structures

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1. Abstract

Blistering of 11 nm and 45 nm-thick Al_2O_3 layers deposited by ALD on silicon substrates is studied for Al- Al_2O_3 -Si structures fabricated using a field isolated process. Blisters are shown to be unevenly distributed and with different dimensions. After chemical etching down to silicon, round voids are revealed underneath the blisters.

2. Introduction

Atomic Layer Deposition (ALD) of Al_2O_3 layers on silicon has attracted increasing attention. Among different applications, it has been shown that Al_2O_3 films are of interest for surface passivation in crystalline silicon solar cells [1,2]. In this technology, high-temperature processes after the oxide deposition are carried out which may cause blistering of the layer [3]. This phenomenon can prevent the use of the layers, particularly when the blister height is large and photolithography steps are necessary. We have already reported [4] a thorough analysis of the conditions under which blistering appears and of the blister characteristics. Similar results have been reported [5,6] although little attention was paid to the effect of the blistering on the silicon surface. In [4] we showed that, in the case of Aluminum capped Al_2O_3 , not only blistering was observed but also silicon voids were detected after chemical etching of Al and Al_2O_3 . In the present work, we study the effect of a post-deposition thermal treatment on the blistering of Al_2O_3 layers of different thickness and its effect on the silicon surface in Al- Al_2O_3 -Si structures.

3. Experimental

The starting material used in this work is p-type Czochralski (100) silicon, with resistivity in the range of 0.1-1.4 $\Omega\cdot\text{cm}$. Al- Al_2O_3 -Si capacitors were fabricated using a field isolated process, forming square active areas. Before Al_2O_3 processing, the wafers were cleaned in a $\text{H}_2\text{SO}_4+\text{H}_2\text{O}_2$ solution followed by a HF(5%) dip; therefore, all the deposition processes were performed on a hydrogen-terminated silicon surface. The studied Al_2O_3 layers were grown in a Cambridge NanoTech Savannah 200 system, using Trimethylaluminium and H_2O as precursors, and N_2 as carrier and purge gas. Al_2O_3 layers grown by means of 100 and 400 ALD cycles, leading to a thickness of 11

nm and 45 nm, respectively, were analyzed. After deposition an annealing step at 650°C in N_2 for 30 min was done. Next, a 500 nm-thick Al/0.5%Cu layer was deposited and patterned to define the metal gate of the Al- Al_2O_3 -Si structure. Finally, the wafers underwent a post-metallization annealing in forming gas ($\text{N}_2/(10\%)\text{H}_2$) at 350°C for 20 min.

After fabrication, optical inspection was used to assess the distribution and characteristics of the blisters. In order to evaluate the condition of the silicon surface, the Al and Al_2O_3 layers were etched off by means of a commercially prepared defreckling aluminum etch (DAE) acid. SEM imaging together with EDX analysis were used to analyze the revealed surface.

3. Results and discussion

Optical inspection of the fabricated samples confirmed that blistering is only observed in the areas corresponding to Al- Al_2O_3 -Si, i.e., no blistering occurs when Al_2O_3 is deposited on the SiO_2 field oxide, indicating that blistering is related to adhesion of Al_2O_3 on Si. In addition, as shown in Fig.1, the dimensions and distribution of blisters are not uniform, even for structures of the same area.

After etching off the Al and Al_2O_3 layers, round silicon voids were observed on the silicon surface. The exact correspondence between the blisters and the silicon voids has been verified by SEM with the aid of fiducial marks done by FIB (Fig.2). A close analysis of the silicon voids shows that the round edge is extremely vertical and well-defined (Fig.3), which is an indication of the chemical nature of the effect rather than a consequence of mechanical stress. Since these silicon voids are only observed when the Al_2O_3 layer is capped with Al, this can be an indication of some chemical reaction at the Si surface underneath the blister. In all cases, EDX spectra indicated that only silicon is present in the surface of the samples after etching.

References

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Fig.1. Optical image of the distribution of blisters in two 980x980 μm^2 Al- Al_2O_3 -Si structures of the same wafer, for 45 nm-thick Al_2O_3 .

Fig.2. SEM image of (a) the aluminum surface showing the blisters and (b) the silicon surface after etching the Al and Al_2O_3 layers, corresponding to the 45 nm-thick Al_2O_3 . The crossed bars patterns were done by FIB etching as a fiducial.

(a)

(b)

Fig.3. SEM images of the silicon voids revealed on the silicon surface after etching the Al and Al_2O_3 layers in structures with 11 nm-thick Al_2O_3 (a), and with 45 nm-thick Al_2O_3 (b).