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Influence of annealing in H atmosphere on the electrical properties of Al_2O_3 layers grown on *p*-type Si by the atomic layer deposition technique

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ABSTRACT

In the present study the electrical properties of 100 nm and 400 nm alumina films grown by the atomic layer deposition technique on *p*-type Si before and after a post-deposition annealing at 440 °C and after a dc H plasma treatment at different temperatures are investigated. We show that the density of interface states is below $2 \times 10^{10}\,cm^{-2}$ in these samples and this value is significantly lower compared to that reported previously in thinner alumina layers (below 50 nm). The effective minority carrier lifetime $\tau_{g,eff}$ and the effective surface recombination velocity s_{eff} in untreated *p*-type Si samples with 100 nm and 400 nm aluminum oxide is comparable with those obtained after thermal oxidation of 90 nm SiO_2. Both, a post-deposition annealing in forming gas (nitrogen/hydrogen) at elevated temperatures and a dc H-plasma treatment at temperatures close to room temperature lead to the introduction of negatively charged defects in alumina films. The results obtained in samples annealed in different atmospheres at different temperatures or subjected to a dc H plasma treatment allow us to correlate these centers with H-related defects. By comparing with theory we tentatively assign them to negatively charged interstitial H atoms.

1. Introduction

Aluminum oxide thin films, which provide excellent surface passivation of *n*- and *p*-type Si, can be used in different applications of modern microelectronics and photovoltaics. Thin Al_2O_3 layers (<100 nm) are considered as an alternative to standard SiO_2 isolation for the gate electrode in metal–oxide–semiconductor field effect transistors (MOSFET) due to the reduction of the channel length to submicron size. The electrical and structural properties of such layers deposited by atomic layer deposition (ALD), plasma epitaxial chemical vapor deposition (PEC-VD) or RF sputtering were extensively investigated in Refs. [1–10]. However, in some other applications of modern microelectronics, such as capacitive micromachined ultrasonic transducers or bimorph actuators [11–13], Al_2O_3 films with thicknesses of more than 100 nm are required. Such films are especially important in a technology where a HF vapor is employed for etching SiO_2, which is used as a sacrificial layer. In this case, the use of SiO_2 as a standard insulator is not possible and it should be replaced by an alternative material which is resistive to HF vapor etching and thermodynamically stable in contact with Si.

Usually, in microelectronics ambient anneal in forming gas (inert gas/H_2) is used for the passivation of electrically active interface states between Si and SiO_2 [9]. When Al_2O_3 layers are used for passivation a post-deposition thermal annealing is often required to decrease the density of interface states, irrespective of the deposition techniques [3–7]. However, the influence of annealing in forming gas containing hydrogen on the electrical properties of alumina layers is still not well understood. In Ref. [4] Zhang et al. investigated the effectivity of the activation anneals in dependence of the ambient gas in reactively sputtered AlO_x films. Among the different investigates ambient gases a mixture of N_2 and H_2 was found to be most effective for sputtered layers leading to an effective surface recombination velocity of about 5 cm/s. In contrast, annealing in nitrogen atmosphere was found to be beneficial for sputter-deposited alumina films in Refs. [10,14].

It is well-known that the post-deposition annealing of Al_2O_3 thin films leads to the chemical passivation of interface states on one hand and to an increase of the concentration of negative charges in these structures on the other hand [1–10]. The presence of the additional negative charges in the Al_2O_3 films is beneficial for photovoltaic applications due to the reduction of electron concentrations close to the surface by the shielding effect as described in Refs. [3,6]. However, it can be undesirable for the microelectronic devices mentioned above. Therefore, the control over defects at the interface and in Al_2O_3 is of prime technological importance.

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To the best of our knowledge, no reports of the structural and electrical properties of alumina films thicker than 100 nm before and after annealing in ambient gas exist in the literature.

In the present study we compare the electrical properties of amorphous AlO_x layers grown with different thicknesses ($\geqslant$100 nm) on *p*-type Si by the atomic layer deposition (ALD) technique with those additionally annealed in forming gas (nitrogen/hydrogen) or subjected to a dc H-plasma treatment at different temperatures. The ALD technique is chosen because its ability to create thin layers on large wafers with a high degree of homogeneity, reproducibility and a considerably lower defect concentration compared to sputtering techniques. We show that the introduction of H significantly modifies the electrical properties of the films. The origin of the changes is discussed.

2. Experimental procedure

Samples were 150 mm *p*-type Si wafers with a resistivity of about 2 Ωcm. AlO_x thin films with a thickness of 100 nm and 400 nm were deposited by the ALD technique at 300 °C. Trimethylaluminum (TMA) and de-ionized water precursors, which were kept at room temperature, were used as aluminum and oxygen source, respectively. Each precursor flowed separately through the deposition chamber. High purity nitrogen was applied as purging gas. During the growth the pulsing time was 0.2 s for both precursors whereas the purging time was 4 s and 8 s for TMA and deionized water, respectively. The oxide thickness was determined by ellipsometry measurements.

Aluminum contacts with an area of 0.25 mm^2 and 1 mm^2 and a thickness of 500 nm were formed by sputtering at room temperature. Some of the samples were annealed in an ambient gas (hydrogen/inert gas) or argon atmosphere at 440 °C for 30 min and some of them were subjected to a dc H plasma treatment at different temperatures in the range of 50–250 °C for 60 min. The accelerating voltage for the H plasma treatment was 300 V. After each annealing step the samples were rapidly quenched to room temperature.

Stress in the films was measured by the comparison of the wafer curvature before and after the deposition of alumina layers. The curvature was determined by a reflected laser beam and the stress was calculated by the Stoney equation [15,16]. According to the definition, tensile stresses are positive and compressive stresses are negative.

The structural properties of the aluminum oxide films were investigated by X-ray diffraction (XRD) measurements. Current–voltage characteristics were recorded in the range of −170 °C to +27 °C. Capacitance–voltage (*C*–*V*) measurements were performed at different frequencies in the range of 100 Hz–1 MHz at room temperature. Conductance–voltage (*G*–*V*) curves were obtained from impedance measurements at room temperature. The conductance was measured as the equivalent parallel conductance. For bias temperature stress measurements *C*–*V* curves before and after the stress performed with −5 V (for 100 nm) and −20 V (for 400 nm) at 150 °C were compared.

For the electrical characterization capacitance–voltage, impedance, capacitance–time, and current–voltage measurements performed at different temperatures and frequencies are used. In order to determine the effective surface recombination velocity and the effective minority carrier lifetime, capacitance versus time measurements were performed at different temperatures in the range of 30–70 °C. During the measurements the MOS capacitor was pulsed into deep depletion and the capacitance was recorded as a function of time. The effective surface recombination velocity and the effective minority carrier lifetime were calculated as described in Refs. [17,18].

3. Experimental results

Fig. 1 presents high frequency *C*–*V* characteristics recorded in 100 nm and 400 nm Al_2O_3/*p*-type Si samples before and after a post deposition annealing at 440 °C in forming gas and after H plasma treatment performed at 50 °C and 100 °C, respectively. The curves are typical for MOS structures with a saturation of the capacitance in the accumulation regime and a gradual reduction in the depletion region. The dielectric constant of alumina is found from the saturation value of the capacitance as 7 for 100 nm layers and as 9 for 400 nm layers and it is not changed after the annealing in forming gas. The flatband voltage (V_{fb}), which is determined from *C*–*V* curves as described in Ref. [17], shifts stronger towards positive bias in as-grown samples with 400 nm alumina layers compared to those with 100 nm Al_2O_3. The post-deposition annealing at 440 °C in forming gas leads to a further shift of the *C*–*V* curves towards higher biases. We also notice that after the post-deposition annealing the shift of V_{fb} is significantly smaller for 100 nm AlO_x/*p*-type Si structures (see the inset in Fig. 1a) compared to 400 nm alumina, where it even reaches 7–8 V depending on the position of the sample on the wafer. The positive shift of the flatband voltage is usually ascribed to the appearance of additional negative charge in Al_2O_3/*p*-type Si structures.

After annealing the samples at 440 °C in argon atmosphere we also observe a shift of the flatband voltage in all samples investigated (for the sake of clarity not shown in Fig. 1). However, this shift (around 1 V for 100 nm Al_2O_3 and about 6 V for 400 nm Al_2O_3) is slightly smaller compared to that observed in the samples after the post-deposition annealing in forming gas.

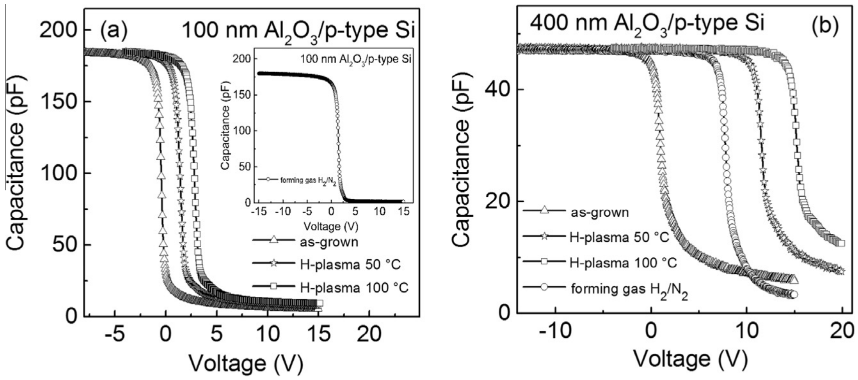

Fig. 1. *C*–*V* characteristics recorded at 100 kHz for 100 nm and 400 nm Al_2O_3 before and after the post-deposition annealing in forming gas at 440 °C and after a dc H plasma treatment at 50 °C and 100 °C.