ANODIC SiO₂ FOR LOW TEMPERATURE GATE DIELECTRICS

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ABSTRACT

Electrical properties of anodic SiO₂ grown at room temperature and annealed at 450°C have been shown to closely approach those of thermal SiO₂. Midgap interface state densities in the low-10¹⁰ cm⁻²·eV⁻¹, oxide surface charge at flatband in the low-10¹⁰ cm⁻², average breakdown fields in excess of 10 MV/cm, and dc resistivities above 10¹⁶ Ω·cm at 1MV/cm have been measured. The oxide surface charge at flatband is thickness dependent. The dependence of electrical and structural properties on various annealing conditions will be discussed.

INTRODUCTION

The trend towards shrinking the dimensions of silicon integrated circuit devices for improved speed and packing density necessitates the reduction in both the thickness and processing temperature of MOS gate oxides. Temperatures of 900-1100°C used in growing conventional thermal gate oxides give rise to several undesirable effects such as broadening of dopant profiles, generation of stacking faults, wafer warpage, and oxidation enhanced diffusion which hinder the performance of small dimension MOS devices. Furthermore, the availability of a good quality, low temperature gate oxide is of utmost importance for amorphous and polycrystalline silicon thin film transistors on glass substrates used for display applications. Therefore, there is a substantial need for the development of low temperature, gate quality SiO₂.

During recent years, there has been a wide range of activities in the fabrication of thin layer of silicon dioxide at low temperatures. A variety of techniques such as plasma-enhanced CVD (PECVD) (1-3), photo-assisted CVD (4-6), laser-enhanced oxidation (7), plasma oxidation (8-10), low temperature CVD (11,12), and sputtering (13) have been employed. Most of these processes result in oxides which are less dense, slightly deficient in oxygen, and have poor electrical and interfacial properties in comparison with the state-of-the-art thermal oxides, even under optimum low temperature anneal conditions. Among these techniques, plasma-enhanced and photo-assisted CVD have resulted in the best quality low temperature oxides. Annealed midgap interface state and flatband oxide surface charge densities in the range of mid-10¹⁰ to mid-10¹¹ cm⁻²·eV⁻¹ and cm⁻², respectively, and mean breakdown fields of 9-10 MV/cm have been reported.
in these two low temperature oxides (1-6). The PECVD process, however, has the disadvantage of heavy substrate damage from charged particles and UV light created in the plasma (8). while the photo-assisted CVD oxides suffer from annealed interface state densities in the low to mid-10¹ⁱ cm⁻²·eV⁻¹ range (4,6) which is more than an order of magnitude higher than those measured in thermal oxides. Furthermore, it is difficult to deposit oxides with thickness uniformities as good as those obtained in thermal oxides using these two techniques.

Besides some early work in the 60’s and 70’s (14-16), little attention has recently been paid to anodic silicon dioxide as a low temperature dielectric (17-19). The purpose of this paper is to investigate the structural, electrical, and interfacial properties of thin layers of SiO₂ grown by anodic oxidation of Si at room temperature with a subsequent low temperature anneal, as well as to examine their suitability for MOS gate oxides. We report here midgap interface state densities as low as 1.7×10¹⁰ cm⁻²·eV⁻¹ together with mean breakdown fields in excess of 10 MV/cm at a maximum processing temperature of 450°C. To our knowledge, this is the lowest reported value of midgap interface state density in any low temperature SiO₂ with a maximum processing temperature below 500°C.

EXPERIMENTAL

Two inch p-type (100) Si wafers with boron doping levels of 1-2×10¹⁵ cm⁻³ were used in this study. The oxides were grown in two different electrolytes: a 0.04M solution of KNO₃ in N-methylacetamide (NMA), and a solution of 0.02M KNO₃ and 0.02M KNO₂ in ethylene glycol (EG). The potassium nitrate (KNO₃) used had a purity of 99.999%, the potassium nitrite (KNO₂) powder was 97% pure, and the two solvents (NMA and EG) were 99% pure. The anodic oxides were grown at room temperature at a constant current density of 2.5 mA/cm² until the desired thickness was reached, and then maintained at the forming voltage for an additional 10 minutes. This procedure has been shown to result in improved interfacial properties (15). For electrical measurements, MOS capacitors with thermally evaporated aluminum gates 635 μm in diameter were constructed. Most of the capacitors received a post-metallization anneal (PMA) step at 450°C in forming gas for one hour before defining the Al dots by photolithography.

The thickness of the anodic oxide films increases linearly with the forming voltage, defined as the difference between the final and initial cell voltages, as previously reported (14,17). Anodic oxide layers were grown on Si in both solutions in the thickness range of 325-1600 Å, corresponding to forming voltages between 35 and 255 V. The thickness uniformities obtained across the 2 inch wafers were better than 1% for both growth solutions, and better than 5% from run to run. This uniformity and reproducibility, which is an inherent consequence of the anodization process, is one the major attributes of this growth technique.

A combination of high frequency (1 MHz) and quasistatic CV measurements were used to extract the interface state and the flatband oxide charge densities. The breakdown fields, leakage currents, and current-voltage characteristics were evaluated using stepped and ramp IV measurements. The structural properties of these oxides as a function various annealing conditions were examined using infrared absorption spectroscopy. The thickness of the oxides grown were measured using Nanospec assuming a refractive index of 1.46. Secondary ion mass spectrometry (SIMS) was used to determine the purity of the anodic oxides.

STRUCTURAL PROPERTIES

Stoichiometric SiO₂ exhibits 3 characteristic absorption bands near 1075, 800, and 450 cm⁻¹ which are due to the stretching, bending, and rocking motions of the Si-O bond, respectively (20). These band shift towards lower frequencies as the oxide moves off stoichiometry and becomes deficient in oxygen (21). or