Etching Mechanism and Plasma-Induced Damage of High-k (Ba,Sr)TiO3 Thin-Film Capacitors

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ABSTRACT

Recently, much attention has been paid to (Ba,Sr)TiO3 (BST) thin films due to its high permittivity for application of Gbit dynamic random access memories and integrated decoupling capacitors. However, the leakage current of BST has been reported to drastically increase, when the film thickness is reduced to less than 20 nm. Now, although the BST could provide significant potential for improving device performance, simplifying structures and shrinking device sizes, several problems must be overcome for applications to be realized. These include improvement of the physical and electrical properties of the film and development of a process for dry etching of the BST films or electrode materials. In this study, the plasma treatment to reduced the leakage current and dry etching process of BST films in an inductively-coupled-plasma (ICP) was investigated. A Langmuir probe was also used to characterize the plasma. As a result of the exposure of (Ba,Sr)TiO3 to the NH3 plasma, the leakage current density of the (Ba,Sr)TiO3 capacitor can be improved by two orders of magnitude as compared that of the non-plasma-treated sample at an applied voltage of 1.5 V. The improvement of leakage properties of (Ba,Sr)TiO3 films can be attributed to the nitrogen incorporation that reduce the oxygen vacancies. From the x-ray photoelectron spectroscopy examination, the existence of N 1s peak was observed in the plasma-treated sample. However, the dielectric property may be damaged by the plasma-induced space charge or ion bombardment. It will induce additional space charges and results in the reduction of the dielectric constant. The competition of nitrogen incorporation into the oxygen vacancies and plasma-induced damage could be considered the main effect of the nitridation of (Ba,Sr)TiO3 films in ammonia plasma. The etching behavior of Ba0.7Sr0.3TiO3 (BST) thin films has been characterized with Cl2/CF4, Cl2/SF6 and Cl2/Ar gas mixtures. The reactivity of BST was initially estimated by thermochemical calculations. CF4 and SF6 were found to impede the etch process, presumably due to competition between plasma deposition and etching. A chemically assisted etch of BST was obtained under various Cl2/Ar gas mixtures. The etch profile along with etch anisotropy was observed as a function of etching parameters by scanning electron microscopy. A smooth surface (roughness ~1.8 nm) with no residue was observed under 30% Cl2 in Ar/Cl2, ICP power of 800 W, RF power of 100 W , and 5 mTorr. To clarify the etching mechanism, the surface reaction of the BST thin films was investigated by X-ray photoelectron spectroscopy. It was found that Ba was mainly removed by chemically assisted physical etching (possible products such as BaClx). Physical bombardment is more effective than Cl chemical reaction for removing Sr, while Ti can almost be removed by chemical reaction (such as TiClx). The etching results described correlate well with the thermochemical calculations. However, the etching process may induce plasma damage, quantitative analysis of the etching damage was attempted to discuss the mechanism of leakage current density and dielectric constant with various RF power and ICP power on Pt/BST/Pt capacitor. In this study, this damage can be effectively recovered with annealed at around 600°C in oxygen ambience and the leakage current density is less than 3×10-7 (A/cm2) under applied voltage of 1.5 V, while its capacitance corresponds to the SiO2 equivalent thickness of 3.5 nm.

Keywords : (Ba ; Sr)TiO3 (BST) ; High-k material ; Thin-Film Capacitor ; inductively Coupled Plasma (ICP) ; Etch ; Plasma-induced damage

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