4 Oxidation of H-Terminated Silicon

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4.1 Introduction

Recently, the densities, functions and operating speeds of integrated circuits driven by ever-increasing numbers of metal-oxide–semiconductor field-effect transistors (MOSFETs) have increased remarkably to produce not only ultrahigh-speed computers, but also many intelligent operating systems. This is largely a result of continuing progress in Si single-crystal growth and Si-related process and microfabrication technologies for integrated circuits. It is made possible by the stable electrical and thermal properties of Si-SiO$_2$ systems and the abundant silicon resources on the earth.

In 1987, MOSFETs with a gate oxide film thickness of 3.3 nm were shown to operate at liquid nitrogen temperature [1]. Later, MOSFETs with a gate oxide film thickness of 1.5 nm were shown to operate at room temperature [2]. More recently, Muller et al. placed a fundamental limit of 0.7 nm on the thinnest usable silicon dioxide gate dielectrics [3]. Interface roughness realized by current oxide growth techniques raised this limit to 1.2 nm. However, the following fundamental facts continue to pose problems: (1) the maximum flatness of the Si(100) surface determines the maximum flatness at SiO$_2$/Si interfaces; (2) the maximum flatness at the interface determines the minimum interface state densities; and (3) for the formation of ultrathin silicon oxide at high temperatures a H-Si surface is superior to a chemically cleaned surface, which is usually covered with chemical oxide. Because the thickness of gate oxide film used in the most advanced MOSFETs is similar to the thickness of the structural transition layer formed on the SiO$_2$ side and since the density of electronic defects in this structural transition layer is always larger than that in bulk SiO$_2$, the quality of the gate oxides is governed by the quality of the structural transition layer. Therefore, it is extremely important to form a high-quality structural transition layer by the atomic-scale control of SiO$_2$/Si [4].

Hydrogen termination by chemical treatment, which has been used to achieve atomically flat Si surfaces, not only promoted the atomic-scale observation at atmospheric pressure, but also initiated the industrial use of atomically flat Si surfaces. This is because the formation of native oxides can be suppressed by terminating the Si surface with hydrogen atoms [5,6]. An atomically flat H-Si(111)-1×1 surface can be obtained by treatment [7] in...
40% NH₄F solution or in boiling water [8], while an atomically flat H-Si(100)-2×1 surface can be obtained by annealing in a hydrogen atmosphere under pressures higher than 0.2 Torr at 700°C [9] or by annealing in a hydrogen atmosphere with a pressure of 1 bar at high temperatures (> 1100°C) [10]. If the H-Si surface can be oxidized without breaking Si-H bonds, the flatness of the Si surface will be roughly preserved. From a study on the stability of approximately one-molecular-layer-thick oxide (abbreviated as preoxide hereafter) formed on a Si(100) surface at 300°C without breaking Si-H bonds, it was found that the preoxide is stable up to 900°C in dry argon gas [11]. Therefore, in the present study preoxide was used in order to keep the oxide surface smooth even during high-temperature oxidation. The initial stage of oxidation of H-Si surfaces was studied by multiple internal reflection infrared absorption spectroscopy (MIR-IRAS) and X-ray photoelectron spectroscopy (XPS) (Sect. 4.3).

The layer-by-layer oxidation process on the Si surface was first discovered using a transmission electron microscope [12] and was later confirmed on an atomic scale in the lateral direction using a scanning reflection electron microscope [13,14]. This layer-by-layer oxidation reaction at the interface is inferred from XPS studies on the interface structures (Sect. 4.4). Indeed, on the Si(111) surface, periodic changes in interface structures appear as a result of the bonding nature of the Si crystal at the interface [15]. An abrupt compositional transition takes place on Si(111) and (100) surfaces and is weakly affected by the atomic steps on the initial surface [16].

In order to reduce the oxidation-induced stress near the interface, structural transition layers are formed on both sides of the interface. The thickness of this structural transition layer on the oxide side was determined to be about 1 nm from an analysis of infrared absorbance and X-ray reflectance [17,18]. A valence band discontinuity of 0.2 eV was found at the boundary between this structural transition layer and the bulk SiO₂ layer for oxides formed on Si(111) and Si(100) [19,20] and was shown to result from the distortion of silicon oxides in the structural transition layer [21,22]. Furthermore, differences between the structural transition layer and the bulk SiO₂ layer were established by measuring the O 1s photoelectron energy loss spectra; this is probably because there is a large difference in defect structure between these two layers [23,24]. This can be expected from the recent medium-energy ion-scattering studies in which the oxidation reaction occurs not only at the interface but also near the interface [25]. The reduction of oxidation-induced stress near the interface is important, but will not be further discussed here.

The morphology of oxide surfaces is discussed in Sect. 4.5. In fact, studies on oxide surfaces using non-contact mode atomic force microscopy (NC-AFM) [26,27] have shown that there is a clear difference between the surface morphologies of oxides formed on Si(111) and Si(100). As the thickness of the oxide layer increases from 1.0 to 1.7 nm, the size of protrusions on the surface of oxides formed on Si(111) increases, while the size of protrusions