



New model for low-temperature oxidation of copper single crystal



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ABSTRACT

Low-temperature oxidation of a copper single crystal, Cu(1 1 1), was investigated using an in situ spectroscopic ellipsometer. The oxidation rate followed the cubic rate law at 5–25 nm oxide thickness; thus, the rate law of Cu single crystal oxidation depended on Cu oxide thickness. Furthermore, the activation energy was found to be close to that of grain boundary diffusion of metal ions in the oxide layer. These results could be explained by grain boundary diffusion and oxide grain growth. Thus, we verified that the low-temperature oxidation kinetics of copper depend on oxide grain growth.

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1. Introduction

With the continuing development of the semiconductor industry, materials that can extend the lifespan of electronic devices and provide improved technical capabilities are in demand. For example, copper is widely used as an important interconnection material for ultralarge-scale integration (ULSI) devices because of its remarkable electric conductivity and resistance [1,2]. However, the use of copper poses a problem of time dependent dielectric breakdown (TDDB), which involves loss of contact between wire and the oxide film and can degrade the products [3–6]. Moreover, copper oxide has a characteristic band gap and is therefore used in devices such as solar cells [7–9]. Copper and its oxide are also regarded as catalysts [10,11]. Realization of these intrinsic characteristics requires surface stabilization of materials; however, to date, no method has been established to achieve this.

To obtain materials with stable surfaces, the oxidation mechanism must be clarified. Studies on low-temperature oxidation have noted that the activation described by the Wagner theory [12] is not applicable, and the force driving the oxidation is not yet clear [13]. Thermal activation, which allows diffusion of atoms and ions, is considered to be absent in an oxidation system at low temperature. Although metals have been observed to oxidize at low temperature, the kinetics and mechanism of this oxidation process are unknown.

Because the Wagner theory cannot be adopted, various other theories have been suggested for the analysis of low-temperature oxidation kinetics [14–20]. Most of these theories are based on the Cabrera–Mott theory [14], and they describe the rate-limiting reactions as the generated electric field [14], tunneling effect [15], and adsorption of oxygen [16]. Most experimental reports indicate that low-temperature oxidation obeys the Cabrera–Mott theory.

At high temperature, ions exhibit thermal activity, and a limiting reaction of oxidation is the transportation of ions through an oxide film. Thus, high-temperature oxidation follows the parabolic law according to the Wagner theory. On the other hand, at temperatures below 700 K, oxidation kinetics does not follow the parabolic law of the Wagner theory, and the oxidation rate is initially very rapid but subsequently becomes slow. The theory proposed by Cabrera and Mott suggests that ion diffusion is promoted in response to the influence of the electric field generated between adsorbed oxygen on an oxide surface and the beneath metal. However, when an oxide film is very thin and the effect of the electric field is large, the migration of ions is not proportional to the electric field; a dominant reaction of oxidation is the escape of ions from the metal. Thus, the oxidation rate follows the inverse logarithmic law. On the other hand, when the film becomes thicker and the effect of the electric field becomes small, the dominant reaction is diffusion of ions through the oxide film in proportion to the electric field and not escape from the metals. Thus, the oxidation rate follows the cubic law. Moreover, similar to the Cabrera–Mott theory, the widely accepted Uhlig theory suggests that the logarithmic law is followed when the diffusion is influenced by a space charge layer [19].

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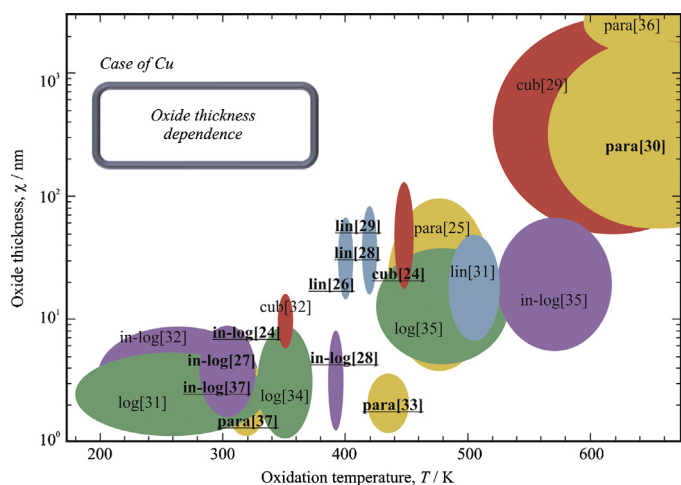


Fig. 1. Relationship among oxidation temperature, oxide thickness, and oxidation rate law in the reported studies on low-temperature copper oxidation. “lin,” “para,” “cub,” “log,” and “in-log” indicate linear law, parabolic law, cubic law, logarithmic law, and inverse-logarithmic law, respectively. The underlined results show experiments with ellipsometry.

Such fundamental theories have been proposed and various theoretical and observational low-temperature oxidation studies of several metals, for example, Cr [21], Ni [22,23], Cu [24–37], and Zn [38,39], have been conducted. Most studies have referred to the low-temperature oxidation using copper, but those experimental results have little coherence. The Cabrera-Mott theory predicts that the thickness of the copper oxide layer grows according to the inverse logarithmic law up to 7.3 nm and according to the cubic law up to 1.5 μm at temperatures of up to 323 K [14]. While some researchers such as Rhodin [32] believed that their experimental results of low-temperature oxidation agreed with the Cabrera-Mott theory, Raugh [26] and Derin [28] reported that oxidation kinetics of copper followed the linear law. We have summarized the oxidation rate law reported by many researchers in Fig. 1. It is noted that the oxidation rate law depends on oxidation temperature, oxide thickness, and so on. Especially, researchers working on low-temperature oxidation have focused on temperature and thickness. In Fig. 1, the x and y -axes represent the oxidation temperature and the oxide thickness, respectively. “lin,” “para,” and “cub” indicate linear law, parabolic law, and cubic law, respectively. Moreover, “log” is a decadic logarithmic law:

$$x = A \log(t) + C \quad (1)$$

“in-log” means an inverse logarithmic law:

$$\frac{1}{x} = A \log(t) + C. \quad (2)$$

The circles and ellipses indicate the range in which each oxidation rate law is followed. For example, Young Jr. [24] indicated that the oxide thickness in the range from 10 to 100 nm measured at 451 K grew according to the cubic law. The conventional theories explained that the low-temperature oxidation followed the inverse logarithmic law or logarithmic law. However, as indicated in Fig. 1, the theoretical and experimental results do not agree. Moreover, different results have been reported even when the experiments were carried out under similar experimental conditions.

Although Rhodin supported the Cabrera-Mott theory, as mentioned above, he determined experimentally that the oxide thickness grew according to the inverse logarithmic law up to 5 nm and then grew according to the cubic law from 78 K to 323 K [32]. Young et al. found that the oxide thickness grew according to the inverse logarithmic law from 343 K to 451 K [24].

Moreover, Young et al. found that the qualitative agreement of their observations with the Cabrera-Mott theory was good, but the quantitative agreement was poor; their oxidation rate constant completely differed from the theoretical constant. Hence, they discussed that the quantitative error was detected because the morphology of the formed oxide and the orientation of metal substrate were not considered in the theory. They explained that the cause of the difference was because previous theories such as the Uhlig theory and Cabrera-Mott theory assume a uniform oxide film on the metal [24]. However, the measurement of low-temperature oxidation is very difficult since the formed oxide is thin and shows poor reproducibility. Poor reproducibility is considered to be due to the complexity of the low-temperature oxidation mechanism, which is affected not only by the oxidation temperature and oxygen partial pressure but also by the purity of the specimens and their microstructure [40]. Some reports indicated that the morphology and/or impurities of specimens greatly influence the oxidation mechanism and thereby change the oxidation rate [40].

Recently, methods for measuring a thin oxide film have been developed. Since the oxide film formed in low-temperature oxidation is extremely thin, the gravimetric measurement often used for high-temperature oxidation research generally causes errors [41]. Although the quartz-crystal oscillator method [42] has been used for many years, its measurement error can become large because it does not measure the actual formed film and it is an indirect measurement method. Measurement of a film thickness using scanning electron microscopy (SEM) or transmission electron microscopy (TEM) requires complicated pretreatments [30], which can destroy the experimental sample. For the initial oxidation stage, it is difficult to perform a preliminary treatment because the oxide film is very thin, and therefore, the true kinetics cannot be determined without using a successive and in situ observation. On the other hand, ellipsometry [24,26,28,33,43] is very useful because it is highly accurate like electron microscopy and can be used for in situ contiguous measurement; spectroscopic ellipsometry [29,30] offers particularly high accuracy.

However, the experimental results often vary even when using the highly accurate ellipsometry technique for low-temperature oxidation measurement. The experimental results obtained using ellipsometry are shown as the underlined rate law in Fig. 1. Different results were obtained for similar oxidation conditions. This can be attributed not only to the continuity of in situ measurement but also to the influences of impurity, morphology, and microstructure of the specimen. Another cause is that the experimental data were insufficient to determine the rate law. In order to acquire the accurate kinetics, it is necessary to solve the problems that cause variations in the experimental results. In light of these findings, the present study aimed to clarify the low-temperature oxidation kinetics of a copper single crystal by solving problems encountered in previous research and by using reliable data. The problems described above have been solved using the following techniques: (i) The influence of impurities and specimen microstructure was reduced using a high-purity single crystal. (ii) The native oxide layer was removed using Ar sputtering for the specimen before oxidation. (iii) In situ spectroscopic ellipsometry was used because it is considered suitable for studying oxidation kinetics. (iv) More reliable data were obtained for the analysis than in previous reports to clarify the oxidation mechanism.

As the oxidation temperature for low-temperature oxidation, Cabrera and Mott discussed their assumption using the experimental data at 373–523 K [14]. Uhlig carried out the verification for his theory at 423–523 K [19]. Fhlner defined the low-temperature oxidation range as near 298 K [13]. Besides, many researchers compared their results with those of Rhodin and Young’s experiment at 78–353 K [32] and 343–451 K [24], respectively. On the basis of

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