International Journal of Applied and Natural Sciences (IJANS);
ISSN(P): 2319-4014; ISSN(E): 2319-4022;
Vol. 4, Issue 6, Oct - Nov 2015; 51-56
© IASET

International Academy of Science, Engineering and Technology
Connecting Researchers; Nurturing Innovations
IASET

# DRY-OXIDATION RATE OF Si(100) SURFACE UP TO 2 nm-OXIDES THICKNESS

**Y. ENTA, M. ARITA & M. WADA**

Graduate School of Science and Technology, Hirosaki University, Hirosaki, Japan

## ABSTRACT

The oxidation rate of a Si(100) surface at oxide thicknesses up to ~2 nm has been measured using chemical-state-resolved x-ray photoelectron spectroscopy in a wide range of oxidation temperature (300 - 850 ºC) and oxygen pressure (10-6 - 1 Torr). The rate curves show very rapid oxidation at the initial stage under all oxidation conditions. The thickness of this initial rapid oxidation depends on the oxidation temperature as well as the oxygen pressure. The data in this regime are not explained by the standard oxidation model and give very important information on the formation of silicon gate oxides in highly integrated metal-oxide-semiconductor field-effect-transistor devices.

**KEYWORDS:** Chemical Shift, Core-Level Photoelectron Spectroscopy, Dry Oxidation, Gate Insulator, MOS FET, Oxidation Rate, Silicon Oxide, Ultrathin Oxide Layer

## INTRODUCTION

The oxidation of silicon has often been described in terms of the Deal-Grove (DG) model [1], which assumes two reactions, the diffusion of oxidant through the growing silicon oxide layer toward the silicon substrate and the actual oxidation occurring at the interface between the oxide and the substrate. This model well reproduces experimental data for oxidation rates when oxide thicknesses are above ~20 nm. However, for thicknesses under 20 nm thickness that are now of critical importance in technology and for the specific case of dry oxidation, the DG model cannot explain the observed rate curves, which show a very fast initial oxidation not predicted by it [1]-[2]. The oxidation kinetics in this fast regime has been extensively studied, but is still controversial. Accurate experimental data are thus needed to better understand and exploit this oxidation regime. While Massoud et al. [3] reported data for the oxidation rate between a few and a few-tens of nm in detail, there was no experimental data below 2 nm. Since current metal-oxide- semiconductor devices require very thin silicon gate oxides below 10 nm thickness, understanding the oxidation rate below a few nm becomes increasingly more important. In previous studies, we performed real-time ambient-pressure x-ray photoelectron spectroscopic (XPS) measurements, and investigated the oxidation rate of a Si(100) surface at oxide thicknesses up to ~2 nm by chemical-state-resolved Si 2p core-level spectra [4]-[5]. In comparison with ellipsometry, this method has high sensitivity to the surface and thus gave us the thickness of the thin oxide with 0.1 – 0.2 nm precision. As a results, we have revealed an existence of a very rapid oxidation regime just at the beginning of oxidation, which is impossible to explain even by Massoud model. However, the oxidation temperature and oxygen pressure in the studies were limited to the narrow range of 300 – 530 ºC and 0.01 – 1 Torr, respectively, and thus the data are not enough to clarify the behavior of the oxidation rate in nanometer thickness. In this study, therefore, we investigate the oxidation rate in a wide range of oxidation temperature (300 – 850 ºC) and oxygen pressure ($10^{-6}$ – 1 Torr), and confirm the existence of the rapid oxidation regime. Cui et al. proposed the rapid oxidation is dominated by the space charge induced by x-ray irradiation [6]. Therefore, we also investigate the space-charge effect by measuring a dependence of the oxidation rate on x-ray irradiation.

## EXPERIMENTAL

The silicon substrate was a mirror-polished, B-doped Si(100) wafer cut to a size of 20×5×0.5 $mm^3$. The wafer was chemically treated to passivate the surface and then annealed by resistive heating at 1000 ºC in an ultrahigh vacuum chamber. The cleanliness of the surface was checked by the surface state in valence-band and Si 2p core-level spectra, which showed no contamination. The XPS measurements were carried out with synchrotron radiation derived from Beam line 3B at Photon Factory, the High Energy Accelerator Research Organization. The dry oxidation was done with 99.99% oxygen gas, which was introduced into the chamber through a variable leak valve. The overall instrumental energy resolution was estimated at about 0.2 eV. The photon energy was set at 135 eV, where the photoelectron inelastic attenuation length from the Si 2p core level in silicon is minimized, being suitable to measure the spectra of the ultrathin oxide layer.

## RESULTS AND DISCUSSIONS

Figure 1 shows typical Si 2p core-level spectrum of oxide layer on Si(100) grown at an oxygen pressure of $10^{-4}$ Torr and oxidation temperature of 750 ºC for 30 s. The Si 2p spectra of the oxide layers grown under a wide range of the oxidation conditions were deconvoluted by a least-square fitting procedure using the spin-orbit split Voigt functions. All Si 2p spectra consisted of five components: substrate silicon ($Si^0$), three sub oxides ($Si^{1+}$, $Si^{2+}$, and $Si3^+$), stoichiometric oxide, that is, $SiO_2$ ($Si^{4+}$). To obtain the oxidation rate, the oxide thickness D was calculated at each time step by the intensity ratio of stoichiometric $SiO_2$ component $I_{SiO2}$ to Si substrate component $I_{Si}$:

$$D = \lambda_{SiO2} \log\left( C \frac{I_{SiO2}}{I_{Si}} + 1 \right)$$

Where $\lambda_{SiO2}$ is the photoelectron inelastic attenuation length in the oxide and $C$ is a coefficient depending on the photon energy [7]. At the photon energy of 135 eV, the values of $\lambda_{SiO2}$ and $C$ are set at 6.8 Å and 0.5, respectively. Figure 2 shows an overview of the thickness of the oxide layers grown for 10 min as a function of the oxidation temperature and the oxygen pressure. The thickness is smaller at lower temperature and at lower pressure, and for example, the thickness at 1 Torr is 3–4 times as large as that at $10^{-6}$ Torr.

Figure 3 shows a series of the obtained oxidation curves, which are summarized as follows

- The oxidation proceeds very rapidly within the oxidation time of 1min at all temperatures. We refer to this regime as "rapid regime".
- After the initial rapid oxidation, the curves become very gentle. We refer to this regime as "slow regime".
- The oxide thickness of the break point dividing the rapid regime and slow regime is smaller at lower oxygen pressure and at lower oxidation temperature.
- The slopes at the same temperatures in the slow regime are almost independent of oxygen pressure.

Krzeminski et al. have succeeded to fit the experimental data between a few and a few-tens nm with a theoretical model using a reaction rate approach [2], which basically assumes the same oxidation reactions as DG model. However,

our obtained rate curves up to 2 nm thickness show discontinuous behavior and thus cannot be explained even by their model. This indicates a different oxidation mechanism dominates the reaction rate below 2 nm thickness. In fact, we can often see a presence of the initial oxide in many previous reports. This oxide has been interpreted as a native oxide and/or an oxide formed under transitional oxidation condition, and therefore not discussed in detail. Our results demonstrate that this initial oxide is not formed by extrinsic factor but resultant of intrinsic oxidation mechanism. Cui et al. have proposed the rapid oxidation is dominated by the space charge induced by x-ray irradiation [6]. However, in this study x-ray was not irradiated during oxidation, because the spectra were obtained after oxidation. Therefore, it is found that there is the rapid regime regardless of x-ray irradiation.

Figure 4 shows Arrhenius plots of the oxidation rates at the oxygen pressures of $10^{-4}$ – 1 Torr, and the activation energies of the oxidation rates derived from Figure 4 are summarized in Table 1. The activation energies are 0.1 – 0.2 eV with weak oxygen pressure dependence. They will give valuable information to consider new oxidation models for the rapid regime.

## CONCLUSIONS

The oxidation rate of a Si(100) surface at oxide thicknesses up to ~2 nm has been measured using chemical-state-resolved x-ray photoelectron spectroscopy in a wide range of oxidation temperature (300 - 850 ºC) and oxygen pressure ($10^{-6}$ - 1 Torr). The oxidation proceeds very rapidly (rapid regime) within the oxidation time of 1 min at all oxidation temperatures. After the initial rapid oxidation, the curves become very gentle (slow regime). The oxide thickness of the break point dividing the rapid regime and slow regime is smaller at lower oxygen pressure and at lower oxidation temperature. The activation energies of oxidation rates are 0.1 – 0.2 eV with weak pressure dependence. The data in the rapid regime are not explained by the standard oxidation model and give very important information on the formation of the silicon gate oxides in highly integrated metal-oxide-semiconductor field-effect-transistor devices.

## ACKNOWLDGEMENTS

This work was partly supported by JSPA KAKENHI Grant Number 15K04618 and Research Project from Graduate School of Science and Technology, Hirosaki University, and performed under the approval of the Photon Factory Program Advisory Committee (Proposal Nos. 2008G673, 2010G586, and 2012G685).

## REFERENCES

1. B. E. Deal and A. S. Grove, “General Relationship for the Thermal Oxidation of Silicon,” Journal of Applied Physics, vol. 36, pp. 3770–3778, 1965.
2. C. Krzeminski, G. Larrieu, J. Penaud, E. Lampin, and E. Dubois, “Silicon Dry Oxidation Kinetics at Low Temperature in the Nan metric Range: Modeling and Experiment,” Journal of Applied Physics, vol. 101, pp. 064908-1–064908-8, 2007, and references therein.
3. H. Z. Massoud, J. D. Plummer, and E. A. Irene, “Thermal Oxidation of Silicon in Dry Oxygen Growth-Rate Enhancement in the Thin Regime: I. Experimental Results,” J. Electro hem. Soc., vol. 132, pp. 2685–2693, 1985.
4. Y. Enta, B. S. Mun, M. Rossi, P. N. Ross, Jr., Z. Hussain, C. S. Fadley, K.-S. Lee and S.-K. Kim, “Real-time observation of the dry oxidation of the Si (100) surface with ambient pressure x-ray photoelectron spectroscopy,” Applied Physics Letters, vol. 92, pp. 012110-1–012110-3, 2008.

5. M. Rossi, B. S. Mun, Y. Enta, C. S. Fadley, K.-S. Lee, S.-K. Kim, H.-J. Shin, Z. Hussain, and P. N. Ross, Jr., "In situ observation of wet oxidation kinetics on Si(100) via ambient pressure x-ray photoemission spectroscopy," Journal of Applied Physics, vol. 103, pp. 044104-1–044104-4, 2008.

6. H. Cui, C. X. Wang, G. W. Yang, and D. Jiang, "Origin of Unusual Rapid Oxidation Process for Ultrathin Oxidation (<2 nm) of Silicon," Applied Physics Letters, vol. 93, pp. 203113, 2008.

7. F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, and J. A. Yarmoff, "Microscopic Structure of the $SiO_2$/Si Interface," Physical Review B, vol. 38, pp. 6084–6096, 1988.

## APPENDICES

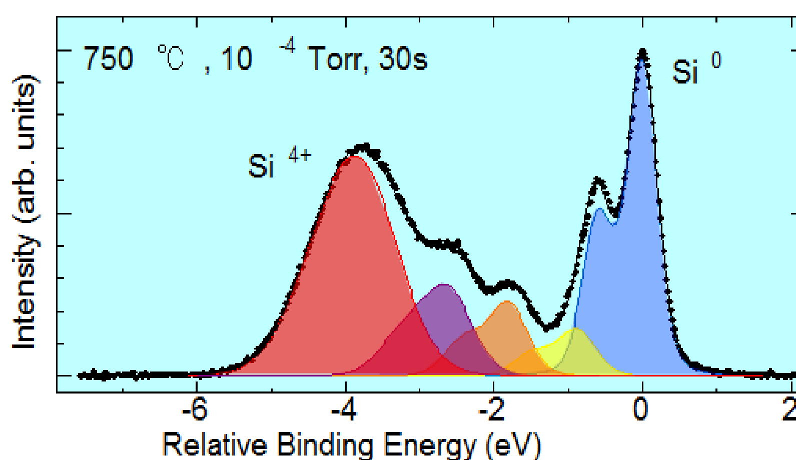


**Figure 1: Typical Si 2p Core-Level Spectrum (Dots) from Oxide Layer on Si (100) Grown at 750 °C and at $10^{-4}$ Torr for 30 s. Solid Lines Denote the Curve Fittings Using The Spin-Orbit Split Voigt Functions**

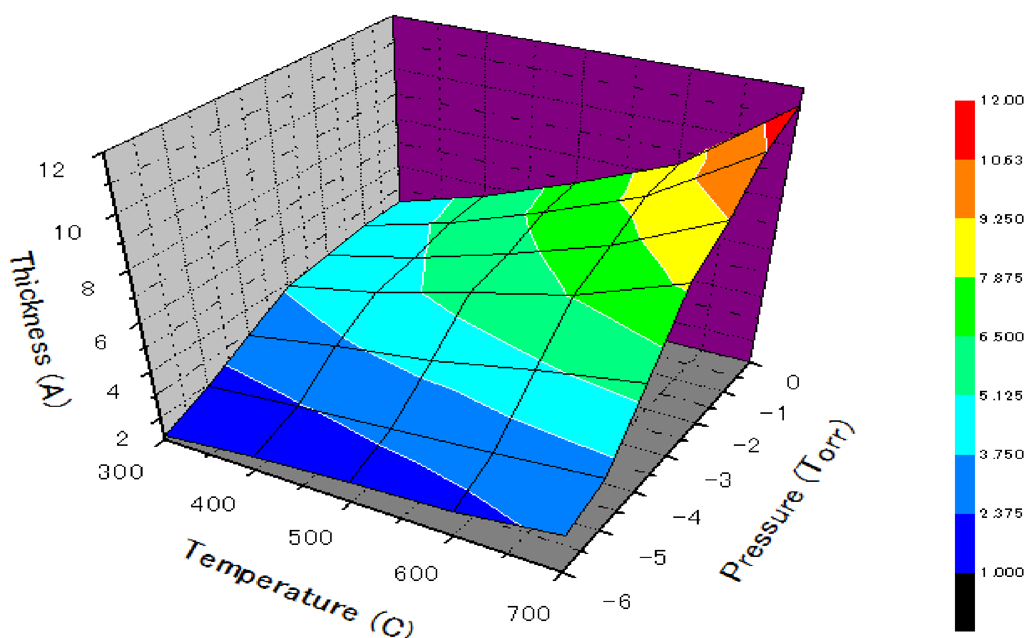


**Figure 2: An Overview of the Thickness of the Oxide Layers Grown for 10 Min as a Function of the Temperature and the Oxygen Pressure**

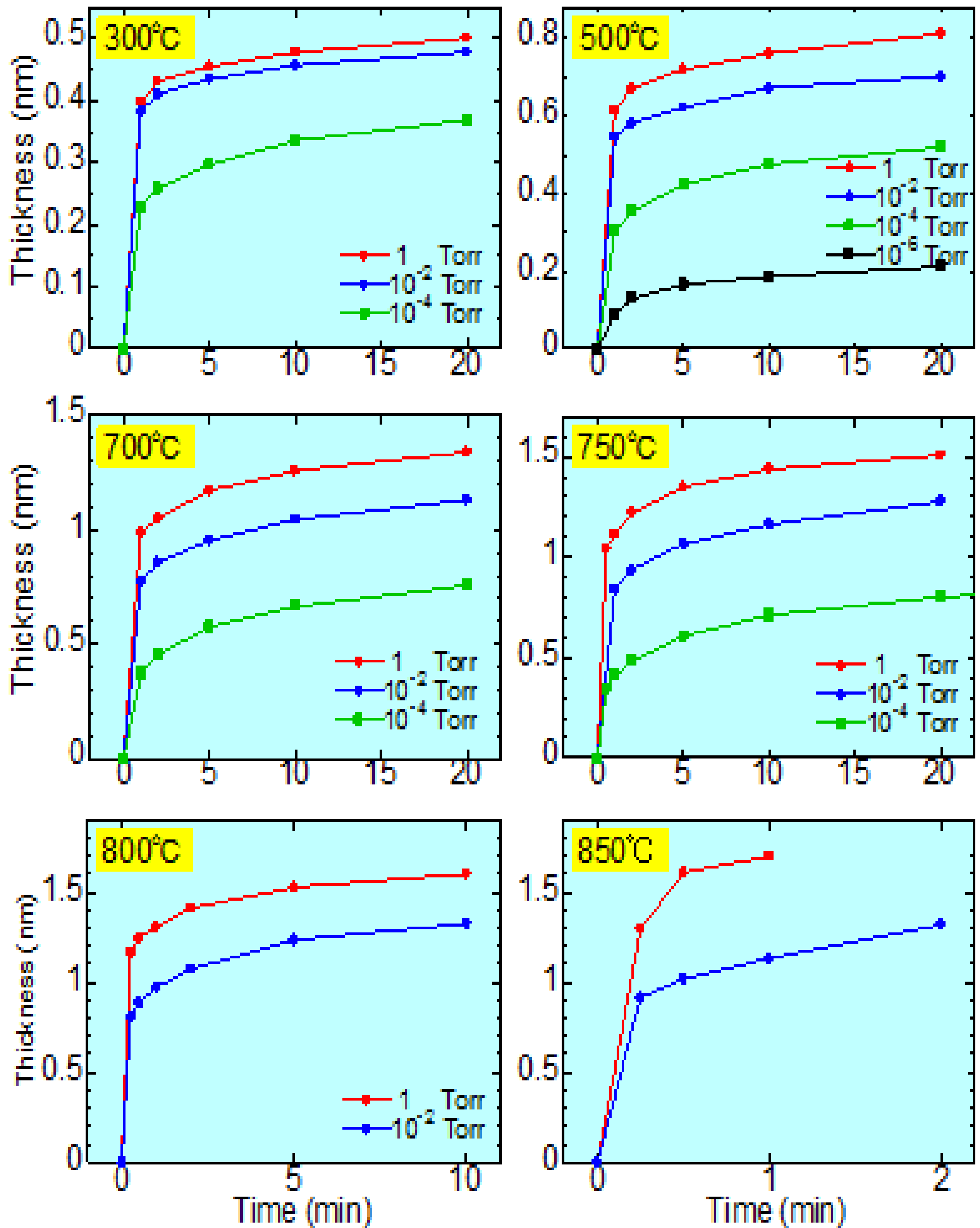


**Figure 3: A Series of the Oxidation-Rate Curves at the Oxidation Temperatures between 300 and 850 °C and at the Oxygen Pressures between $10^{-6}$ and 1 Torr**

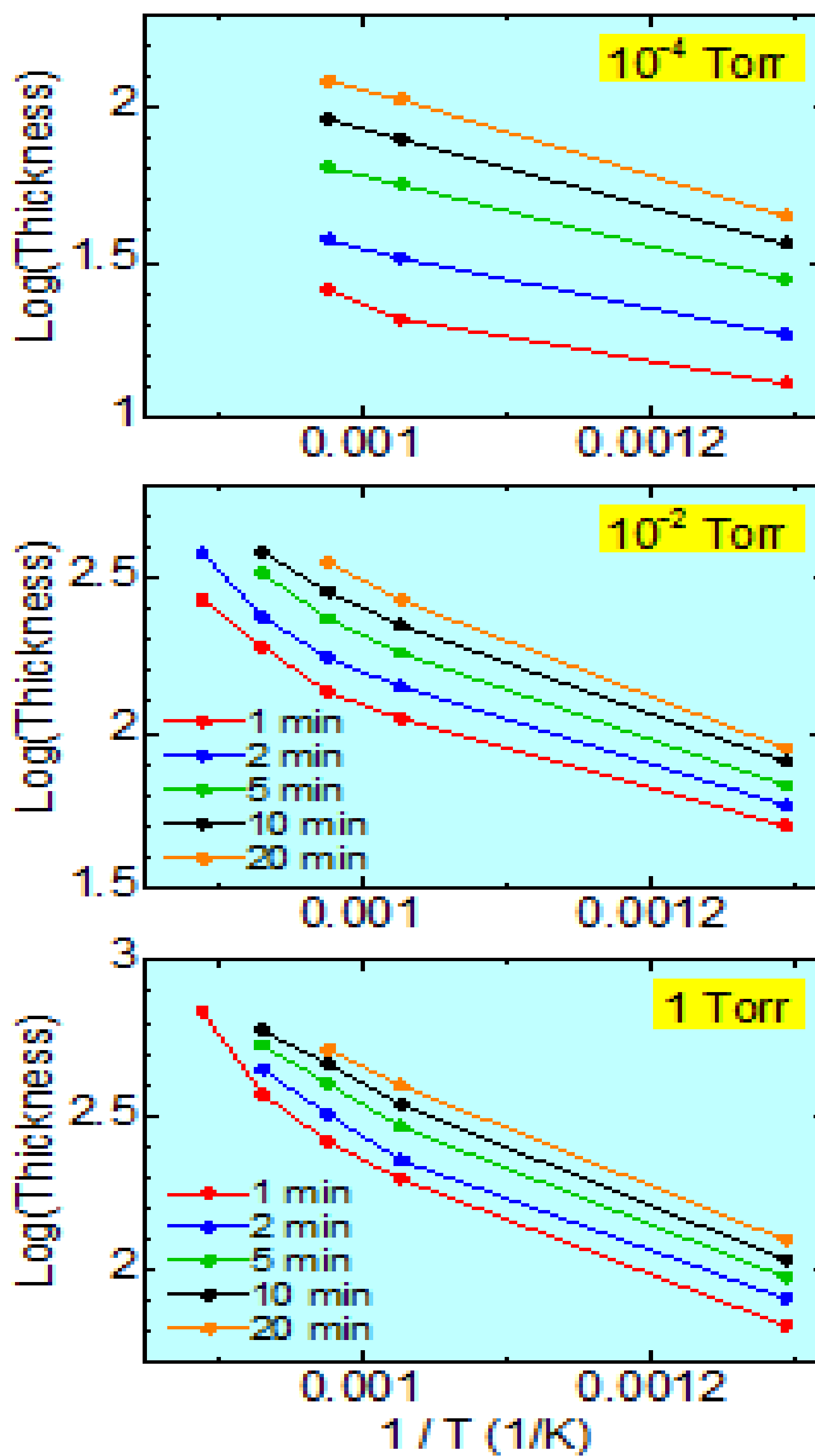


**Figure 4: Arrhenius Plots of the Oxidation Rates at Fixed Oxygen Pressures**

**Table 1: Pressure Dependence of Activation Energy of the Oxidation Rate**

| Pressure (Torr) | $10^{-4}$ | $10^{-2}$ | 1 |
|---|---|---|---|
| Activation Energy (eV) | 0.08 | 0.14 | 0.20 |