



Estimation of activation energies for decomposition reaction of polymer by hydrogen radicals generated using hot-wire catalyzer



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ABSTRACT

This paper discusses the decomposition processes of polymer thin films coated on silicon (Si) substrates by hydrogen radicals generated from H₂ on hot-wire catalyst surfaces. N₂ buffer was used to relax the translational motion of hydrogen radicals. It is shown that H atoms react to polymer films under thermal equilibrium conditions when the total pressure is 21.3 Pa and the distance between the catalyst and the substrate is 100 mm. Polymers with benzene ring such as phenol resin, polystyrene, poly(vinylphenol), and poly(α -methylstyrene) exhibited both low removal rate and high activation energy of decomposition compared to those polymers without benzene ring such as poly(methylmethacrylate) and poly(isobutylene). We concluded that benzene ring with CC bond and resonance structure is resistant to decomposition by hydrogen radicals.

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1. Introduction

In order to fabricate dynamic random access memory (DRAM) and liquid crystal displays (LCDs), thin-film deposition, resist patterning, etching (ion implantation), resist removal, and substrate cleaning are performed over and over again. Resists are often removed by chemicals such as a sulfuric acid–hydrogen peroxide mixture (SPM) and organic amine solutions. These chemicals are expensive and cause environmental damage. To reduce the cost and environmental damage, the development of resist removal methods without chemicals is urgently required in the semiconductor and LCD industries. In resist removal methods without chemicals, ashing using oxygen plasma and ozone gas has been performed, however this approach has several problems. First, the substrate and interconnection are oxidized. Second, device properties are degraded through bombardment by high-energy ions in the plasma. To resolve these problems, we are developing resist removal method using hydrogen radicals [1–11], which are generated by the catalytic decomposition of hydrogen molecules using a tungsten hot-wire catalyzer.

In order to develop resist removal method using hydrogen radicals, it is necessary to clarify the reaction mechanisms between hydrogen radicals and resists (i.e. polymer). Since the development of resist removal method using hydrogen radicals by Izumi and matsumura in 2002 [1], reaction mechanisms were investigated actively [1–3,6,8,11],

but it remains to be explained. The main cause is that reaction between hydrogen radicals and polymers proceeds under the non-equilibrium state. Hydrogen molecules are adsorbed dissociatively onto tungsten dangling bonds of the catalyzer surface. Hydrogen radicals obtain thermal energy from catalyzer heated at 2000 °C or more, and desorb from catalyzer surface. Hydrogen radicals immediately after generation have equivalent energy of “catalyzer temperature – 1000 °C” [12]. On the other hand, the temperature of polymer thin films deposited on substrate is often from 200 to 300 °C. Therefore, reaction between hydrogen radicals and polymer thin films becomes vapor phase/solid phase reaction under the non-equilibrium state, and is difficult to analyze.

In this paper, we apply our developed method that hydrogen radicals react to polymer thin films under the thermal equilibrium state [6], and estimate the activation energies of decomposition reaction of various polymer thin films by hydrogen radicals using Arrhenius's law. In addition, we discuss the decomposition reaction mechanisms of polymer thin films based on the values of activation energies.

2. Experimental

The hydrogen radical irradiation apparatus mainly consists of fused-glass chamber, tungsten hot-wire catalyzer, gas inlet system, substrate holder, substrate heating device, and evacuating system. Schematic of apparatus have presented in our previous paper [6]. The polymer-coated Si substrate was attached just below the catalyzer. The distance

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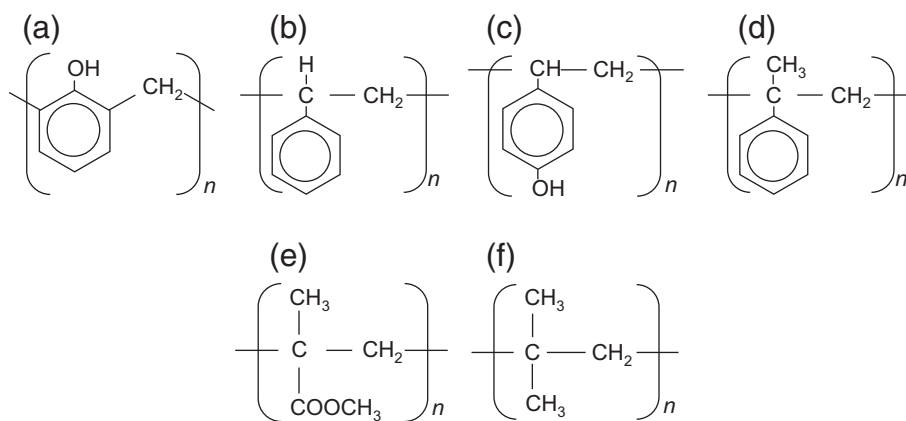


Fig. 1. Chemical structures of (a): phenol resin (Ph), (b): polystyrene (PS), (c): poly(vinylphenol) (PVP), (d): poly(α-methylstyrene) (PMS), (e): poly(methylmethacrylate) (PMMA), and (f): poly(isobutylene) (PIB).

between the catalyzer and the substrate was fixed at 100 mm. The catalyzer was heated at 2400 °C (current = 30 A) using a direct current supply. The catalyzer temperature was measured by using a two-wavelength (0.8 and 1.05 μm) infrared radiation thermometer (Impac Electronic ISR12-L0). H₂/N₂ mixed gas (H₂:N₂ = 10:90 vol.%) was used as the working gas. To avoid explosion, N₂ gas was used by diluting the H₂ gas concentration, and also was used to relax the energy of hydrogen radicals. Energy relaxation mechanism of hydrogen radicals will be described later. The gas flow rate was fixed at 300 sccm using a mass flow controller, and the working gas pressure was fixed at 21.3 Pa (H₂ partial pressure = 2.13 Pa). The initial substrate temperatures (just below the hydrogen radical irradiation) were fixed at 50, 85, and 165 °C. The substrate temperature during hydrogen radical irradiation was monitored using a K-type thermocouple attached to the back of the substrate.

Polymers evaluated are phenol resin (Ph) which was synthesized based on paper reported by Yamagishi et al. [13], polystyrene (PS, Toyo Styrene), poly(vinylphenol) (PVP, Aldrich), poly(α-methylstyrene) (PMS, Wako Pure Chemical Industries), poly(methylmethacrylate) (PMMA, Mitsubishi Rayon), and poly(isobutylene) (PIB, Aldrich). Fig. 1 presents the chemical structures of these polymers. Ph, PS, PVP, and PMS have benzene ring, but PMMA and PIB do not have benzene ring. Polymers were dissolved to each solvent, and then polymer solutions were spin-coated onto a Si wafer (substrate) using a spin coater (Active, ACT-300A) at each rotation speed for 20 s. Polymer thin films after spin coating were baked at 100 °C for 1 min on a hot-plate. Film thickness of polymer thin films was measured using a stylus surface-profile measurement instrument (ULVAC, DekTak 6M). Table 1 presents thin film preparation conditions by spin coating of various polymers. Conditions of Table 1 were designed to obtain the initial film thickness of approximately 1 μm.

The substrate was irradiated with hydrogen radicals while the removal state of polymer thin films was observed visually from the chamber outside. The maximum of single hydrogen radical irradiation time was fixed at 4 min. After the single hydrogen radical irradiation, substrate was cooled to room temperature in an apparatus, and then substrate was retrieved from apparatus to measure the film thickness of polymer thin films. This operation was repeatedly performed until the film thickness of polymer thin films becomes zero. Removal rates of polymer thin films were calculated from slope for removal line of relationship between hydrogen radical irradiation time and film thickness of polymer thin films. In the case where polymer thin films were removed within single hydrogen radical irradiation (within 4 min), removal rates were calculated by dividing the initial film thickness by the hydrogen radical irradiation time at removal completion.

3. Results and discussion

Prior to evaluation of removal rates of polymer thin films, we measured substrate temperature during hydrogen radical irradiation. Fig. 2 demonstrates substrate temperature changes as a function of hydrogen radical irradiation time. Substrate temperatures rose with increasing hydrogen radical irradiation time, and were saturated when the hydrogen radical irradiation time was longer than 2 min. It can be said that substrate is heated by the radiation heat of catalyzer. The saturated substrate temperature increased with higher initial substrate temperature.

Substrate temperatures change against hydrogen radical irradiation time, and so we defined an average substrate temperature T_{ave} by Eq. (1) [6].

$$T_{ave} = \frac{1}{t_{irr}} \int_0^{t_{irr}} T(t) dt \quad (1)$$

In this equation, $T(t)$ is a time-dependent substrate temperature such as the one depicted in Fig. 2. In the case where polymer thin films were removed within single hydrogen radical irradiation of 4 min, “ t_{irr} = hydrogen radical irradiation time at removal completion [min]” was used for calculation. In the case where polymer thin films were not removed within single hydrogen radical irradiation of 4 min, $t_{irr} = 4$ [min] was used. This is based on the following reason. After hydrogen radical irradiation of 4 min, substrate is cooled to room temperature. Therefore, substrate temperature of the next hydrogen irradiation rises in the same way as Fig. 2.

Fig. 3 depicts relationship between average substrate temperature and removal rates of various polymer thin films. For all Ph, PS, PVP, PMS, PMMA, and PIB, removal rates increased with rising average substrate temperature. When average substrate temperature was equal,

Table 1
Thin film preparation conditions by spin coating of various polymers.

Polymer	Mw ^a	Solvent	Polymer concentration (wt.%)	Rotational speed at spin coating (rpm)	Initial film thickness (μm)
Ph	1.0 × 10 ⁴	Ethyl lactate	20	2000	0.98
PS	2.6 × 10 ⁵	Xylene	10	4000	1.05
PVP	2.0 × 10 ⁴	Ethyl lactate	20	3000	1.00
PMS	5.0 × 10 ³	Xylene	15	500	1.00
PMMA	7.0 × 10 ⁴	Ethyl lactate	10	1000	1.00
PIB	4.2 × 10 ⁵	Xylene	10	3000	1.31

^a Weight-average molecular weight.

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