



Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: [www.elsevier.com/locate/tsf](http://www.elsevier.com/locate/tsf)

## Decomposition processes of photoresist polymers by H atoms produced on hot wire surfaces

Hironobu Umemoto<sup>a,b,\*</sup>, Teruto Kato<sup>b</sup>, Masayuki Takiguchi<sup>b</sup>, Seiji Takagi<sup>c</sup>, Hideo Horibe<sup>c</sup>

<sup>a</sup> Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University, Hamamatsu, Shizuoka 432-8561, Japan

<sup>b</sup> Department of Applied Chemistry and Biochemical Engineering, Faculty of Engineering, Shizuoka University, Hamamatsu, Shizuoka 432-8561, Japan

<sup>c</sup> Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan

### ARTICLE INFO

#### Article history:

Received 15 September 2016

Received in revised form 7 December 2016

Accepted 9 December 2016

Available online xxxxx

#### Keywords:

Photoresist removal

Mass spectrometric detection

Catalytic decomposition

Atomic hydrogen

Density functional calculation

### ABSTRACT

Mass spectrometry was used to identify the decomposition products of two typical photoresist polymers, Novolak and polymethylmethacrylate, by H atoms produced on hot wire surfaces. The production of CH<sub>4</sub> and CO was confirmed for both polymers. Other possible products are C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>10</sub> or C<sub>4</sub>H<sub>8</sub>, and some esters such as CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>. The production of CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, alcohols, and aromatics are minor. The possible decomposition mechanisms are discussed on the basis of density functional calculations of the energetics.

© 2016 Elsevier B.V. All rights reserved.

### 1. Introduction

It is now well established that photoresist resins can be decomposed by H atoms produced from H<sub>2</sub> on hot metal wire surfaces [1–5]. Since this method is plasma-free, damage to devices that might be caused by charged particles can be avoided. Ashing by oxidizing gases is a widely used technique for removing photoresists under dry conditions. With this technique, however, oxidation of semiconductor substrates and metal interconnects cannot completely be avoided. With the technique discussed here, resists are removed under a reducing atmosphere and no such problems are expected. The pioneering work on photoresist removal by H atoms was carried out by Izumi and Matsumura in 2002 [6]. They not only measured the removal rates but also identified the decomposition products. They used an electron-bombardment type mass spectrometer and observed some organic fragment ions, such as C<sub>2</sub>H<sub>5</sub><sup>+</sup>. However, the resolution was too low to determine the parent molecules. It is important to know the decomposition mechanisms in order to design and synthesize easily decomposable polymer resins. In addition, the mass spectrometric techniques can be used to determine the end-point of resist removal. For such applications, information on the decomposition products is essential.

In this study, volatile decomposition products of Novolak and PMMA (polymethylmethacrylate) by H atoms were identified using a quadrupole mass spectrometer. Novolak is one of the typical phenolic resins while PMMA is an acrylic resin. Density functional calculations were also carried out to specify the initial decomposition steps. The decomposition mechanism of polymethacrylic esters, including PMMA, by hydrogen plasma was studied by Lub et al. using X-ray photoelectron spectroscopic and static secondary ion mass spectrometric techniques [7]. They analyzed the residual compounds on the substrates but did not analyze the gaseous products. The present study complements their approach.

### 2. Experimental details

The experimental apparatus was similar to that described elsewhere [8–11]. Photoresist polymers (Novolak and PMMA) were dissolved by propylene glycol monomethyl ether acetate (Kanto Kagaku, 99.0%) and painted onto Al sheets. The Al sheet thickness was 0.1 mm, while the size was 1.0 × 10<sup>3</sup> cm<sup>2</sup> for Novolak and 3.0 × 10<sup>2</sup> cm<sup>2</sup> for PMMA. These Al sheets were installed on the inner walls of a vacuum chamber evacuated by a turbomolecular pump (Osaka Vacuum, TG350FCWB). H<sub>2</sub> or He could be introduced into the chamber through a mass flow controller (Horiba STEC, SEC-40 M). H<sub>2</sub> was decomposed to H atoms on a coiled W wire (30 cm in length and 0.39 mm in diameter, Nilaco, 99.95%), which could be resistively heated with a DC power supply (Takasago, EX-1125H2). The wire temperature was measured with a two-wavelength thermometer (LumaSense Technologies, ISR 12-

\* Corresponding author at: Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University, Hamamatsu, Shizuoka 432-8561, Japan  
E-mail address: [umemoto.hironobu@shizuoka.ac.jp](mailto:umemoto.hironobu@shizuoka.ac.jp) (H. Umemoto).

LO). The temperature of the Al sheets, measured with a K-type thermocouple, was  $4.2 \times 10^2$  K when the wire temperature was  $2.42 \times 10^3$  K. A quadrupole mass spectrometer (Canon-Anelva, M-101QA-TDM) was attached to the chamber through a sampling hole. The mass spectrometer was differentially pumped with another turbo molecular pump (Osaka Vacuum, TG220FCAB). The electron impact energy was 70 eV. The mass spectra of authentic samples, such as CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, were measured by using the same apparatus. The mass spectra of the standard samples were similar to the standard mass spectra from the U.S.A. National Institute of Standards and Technology (NIST Standard Reference Database 1A v14), except that the relative signal intensity decreased with the increase in the mass number.

Novolak was produced by Merck Performance Materials Manufacturing, while PMMA was a product of Aldrich. H<sub>2</sub> (Japan Air Gases, 99.999%) and He (Japan Air Gases, 99.999%) were used from cylinders without further purification. The purities of gaseous authentic samples for calibration, such as CO, CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub>, were between 99.0 and 99.9%, while those of liquid samples, such as C<sub>5</sub>H<sub>12</sub>, CH<sub>3</sub>OH, and CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>, were between 95.0 and 99.8%.

### 3. Experimental results

When the wire was heated in the presence of a fresh polymer-painted Al sheet, many mass signals, up to a mass-to-charge ratio of 87, could be observed even in the absence of a H<sub>2</sub> flow. These signals can be attributed to the evaporation of solvent as well as the thermal decomposition of the photoresist polymer. Then, the wire was heated in the presence of a He flow until the signals attributable to organic compounds disappeared. After that, H<sub>2</sub> was introduced to identify the decomposition products formed in the reactions with H atoms. Two wires were installed because carburization cannot be avoided during the preheating. One wire was used for preheating in the presence of He and the other was used to decompose H<sub>2</sub>.

Fig. 1 shows the mass spectrum when Novolak resin was decomposed. The wire temperature was  $2.42 \times 10^3$  K. The pressure and the flow rate of H<sub>2</sub> were 2.3 Pa and 20 sccm (1 sccm =  $6.9 \times 10^{-7}$  mol s<sup>-1</sup>), respectively. Since a weak signal at the mass-to-charge ratio (*m/z*) of 28, attributable to CO<sup>+</sup>, was observed when the wire was heated in the presence of pure He, the subtracted spectrum, [(heated with H<sub>2</sub>) - (unheated with H<sub>2</sub>)] - [(heated with He) - (unheated with He)], is illustrated. No signals assignable to organic compounds could be observed when an Al sheet without coating was installed and the wire was heated in the presence of a H<sub>2</sub> or He flow. The result for PMMA is illustrated in Fig. 2. The wire temperature was  $2.20 \times 10^3$  K. The pressure and the flow rate of H<sub>2</sub> were the same, 2.3 Pa and 20 sccm. In both cases, we could observe intense signals at

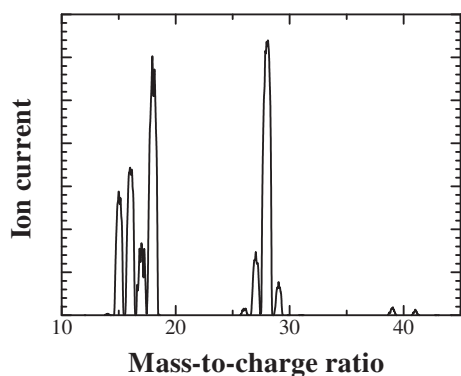


Fig. 1. Mass spectrum when Novolak resin was decomposed. Wire temperature was  $2.42 \times 10^3$  K. H<sub>2</sub> pressure and the flow rate were 2.3 Pa and 20 sccm, respectively. Background signals were subtracted by the procedure described in Section 3.

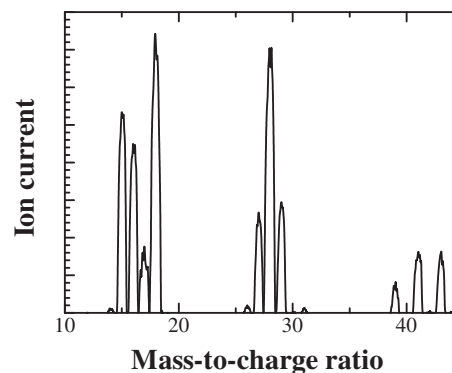


Fig. 2. Mass spectrum when PMMA resin was decomposed. Wire temperature was  $2.20 \times 10^3$  K. H<sub>2</sub> pressure and the flow rate were 2.3 Pa and 20 sccm, respectively. Background signals were subtracted as for Novolak.

*m/z* = 15, 16, 27, 28, and 29, in addition to H<sub>2</sub>O<sup>+</sup> and OH<sup>+</sup> which could be observed as backgrounds. Signals at *m/z* = 14, 30, 31, 42, and 44 were very weak or missing. In the case of PMMA, fairly strong signals could be observed at *m/z* = 39, 41, and 43, while these signals were weak for Novolak. Signals over *m/z* = 50 were very weak.

The mass peaks at *m/z* = 15 and 16 can easily be assigned to CH<sub>3</sub><sup>+</sup> and CH<sub>4</sub><sup>+</sup> produced from CH<sub>4</sub>. The mass spectrum of an authentic sample of CH<sub>4</sub> is illustrated in Fig. 3 together with those of several other samples. The mass peak at *m/z* = 28 suggests the production of CO, while the lack of signals at *m/z* = 44 shows that CO<sub>2</sub> is not produced. The peak at *m/z* = 28 cannot be attributed to C<sub>2</sub>H<sub>4</sub> because the peak at *m/z* = 26 was weak. In the fragmentation of C<sub>2</sub>H<sub>4</sub>, the mass signals at *m/z* = 26 and 27 should be comparable and around half of that at *m/z* = 28. Signals at *m/z* = 27 and 29 as well as the weak ones at *m/z* = 39 and 41 observed in Novolak, may be attributed to C3 or C4 hydrocarbons. The production of C<sub>2</sub>H<sub>6</sub>, C<sub>5</sub>H<sub>12</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, HCOOCH<sub>3</sub>, and CH<sub>3</sub>CHO can be excluded by comparing the mass spectra with those of authentic samples. If C<sub>2</sub>H<sub>6</sub> is produced, a peak at *m/z* = 30 must appear. If CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH or HCOOCH<sub>3</sub> is produced, there must be a characteristic peak at *m/z* = 31, while peaks at *m/z* = 14 and 44 must be observed if CH<sub>3</sub>CHO is produced. If C<sub>5</sub>H<sub>12</sub> is produced, a peak at *m/z* = 42 must appear. Aromatics could not be detected, either.

The characteristic points in the spectrum of PMMA are the signals at *m/z* = 15, 39, 41, and 43. The signal at *m/z* = 15 was more intense than that at *m/z* = 16, and cannot be attributed only to CH<sub>3</sub><sup>+</sup> formed from CH<sub>4</sub>. Strong signals could be observed at *m/z* = 15 and 43, together with those between 27 and 29, when (CH<sub>3</sub>)<sub>2</sub>CO, CH<sub>3</sub>COOCH<sub>3</sub>, or CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub> was ionized, but signals at *m/z* = 39 and 41 were missing.

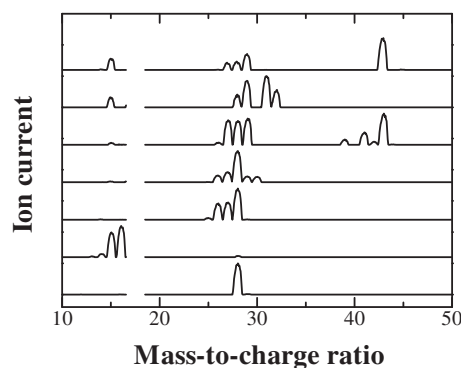


Fig. 3. Mass spectra of authentic samples. Samples were CH<sub>3</sub>COOC<sub>2</sub>H<sub>5</sub>, CH<sub>3</sub>OH, C<sub>4</sub>H<sub>10</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>4</sub>, and CO from up to bottom. These samples were used after being diluted with H<sub>2</sub>. The signals of OH<sup>+</sup> and H<sub>2</sub>O<sup>+</sup> were omitted.

Download English Version:

<https://daneshyari.com/en/article/5465964>

Download Persian Version:

<https://daneshyari.com/article/5465964>

[Daneshyari.com](https://daneshyari.com)