



Organic solvent-free water-developable sugar resist material derived from biomass in green lithography



Satoshi Takei^{a,b,*}, Akihiro Oshima^c, Takumi Ichikawa^a, Atsushi Sekiguchi^a, Miki Kashiwakura^c, Takahiro Kozawa^c, Seiichi Tagawa^c, Tomoko G. Oyama^d, Syoji Ito^b, Hiroshi Miyasaka^b

^a Department of Mechanical Systems Engineering, Toyama Prefectural University, Imizu, Toyama 939-0398, Japan

^b Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

^c The Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567-0047, Japan

^d Quantum Beam Science Directorate, Japan Atomic Energy Agency, Takasaki, Gunma 370-1292, Japan

ARTICLE INFO

Article history:

Received 9 December 2013

Received in revised form 6 February 2014

Accepted 22 February 2014

Available online 1 March 2014

Keywords:

Green lithography

Plant products

Nanofabrication

Organic solvent-free

Water solubility

Etch selectivity

ABSTRACT

We have demonstrated an organic solvent-free water-developable branched sugar resist material derived from biomass for its use in green electron beam lithography. This emphasizes the use of plant products instead of conventionally used tetramethylammonium hydroxide and organic solvents. The rationally designed water-developable branched sugar resist material developed in this study can be patterned with an excellent sensitivity of $7 \mu\text{C}/\text{cm}^2$ and a resolution of 50–200 nm lines. In addition, it indicated sufficient thermal stability at $\sim 180^\circ\text{C}$, acceptable CF_4 etch selectivity with a hardmask material, 42–53% rate of chemical reaction of acryloyl groups affected by the tacticity of branched sugar chain polymers, and developable in pure water at 23°C for 60 s.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nano-fabrications using green lithography encompass the interface of biology and electronics. Conventionally, several techniques, including photolithography, electron beam (EB) lithography, focused ion beam (FIB) lithography, microcontact printing (MCP), and scanning probe lithography (SPL) have been applied to generate user-defined patterned surfaces generated by removal of polymeric resist material from an underlying substrate. Among the different patterning techniques, EB lithography is a maskless procedure by using highly energetic beam of electrons. Next-generation nano-fabrication based on bioelectronics are primarily expected to apply green EB lithography that uses pure water for developing the pattern and a water-developable resist material derived from biomass. Such realization is expected to simplify the procedure adopted for the treatment of liquid waste solvents, such as tetramethylammonium hydroxide (TMAH) water solutions, cyclohexanone and 2-heptanone [1–6]. A sugar chain polymer in biomass compounds is a natural source of alpha-linked

disaccharide formed by 1,1-glycosidic bond between the glucose units.

Nano-fabrications using green EB lithography utilize a water-developable sugar resist material derived from biomass, which will potentially benefit the development of biosensors and bioelectronics by the use of both water solubility and water-development due to avoid the interface damage of biology and electronics. Green EB lithography is also a great substitute for alkaline developer solvents like TMAH and resist solvents, such as cyclohexanone, and 2-heptanone that pose serious safety, health, and environmental concerns. Conventionally, in EB and photo lithography, a resist material is dipped in an aqueous alkaline developer solution of TMAH in pure water [7–10]. The accuracy and reliability of the patterned resist material layer in EB lithography plays an important role in determining the performance of the electronic device [11–13]. To fabricate higher integrated larger-capacity semiconductor and bio-electronic devices, it is necessary to further reduce the linewidth of patterns implementing lithography [14–16]. In some advanced lithography technologies such as EB, nanoimprint, and UV, high sensitivity and film thickness shrinkage by EB or UV irradiation strongly influence resist profiles, patterning dimensional accuracy, and line edge roughness. Recently, film shrinkage of the UV curable branched siloxane, as low-k dielectrics in nanoimprint lithography, has been reported [17]. Furthermore,

* Corresponding author at: Department of Mechanical Systems Engineering, Toyama Prefectural University, Imizu, Toyama 939-0398, Japan. Tel.: +81 766567500; fax: +81 766566131.

E-mail address: takeis@pu-toyama.ac.jp (S. Takei).

UV crosslinkable plant-based resist materials that result in low film thickness shrinkage have been developed in nanoimprint lithography, for realizing environmentally compatible bio-nanofabrication [5,6,18]. In addition, shrinkages of resist materials in EB lithography [19,20], characterization of 157 nm resist polymers [21], and structural changes in the depth direction of ArF resist material have also been investigated [22]. All these studies indicate that the search for prospective resist materials with resolution limit, high sensitivity, and lower film thickness shrinkage, has become necessary for the production of next-generation devices.

On the other hand, the etch selectivity of a fluorinated etch gas in resist material with hardmask layer under the resist material is considered as the key of the etching processes, which use resist materials with lower etch resistance [23–28]. In general, the etch resistance of a resist material is inversely proportional to the Ohnishi parameter, and relates the atomic composition of the polymer, in particular, the number of carbon and oxygen atoms. It is well known that the Ohnishi parameter is useful for estimating etch resistance of an organic material [29–31]. The concentration of oxygen atoms in resist materials with many oxygen atoms is related to the lower etch resistance in resist materials. Therefore, conventional single layer processes are considered to be difficult due to the significant number of oxygen atoms in the proposed water-developable sugar resist material with many oxygen atoms [5,19].

Herein, we have investigated the EB sensitivity, resolution limit, film thickness shrinkage, tacticity of polymers, thermal stability, and etching properties of organic solvent-free water-developable branched sugar resist materials in green EB lithography for developing environmentally-compatible biosensors and bioelectronics by the use of both water solubility and water-development.

2. Experimental method

2.1. Organic solvent-free resist material design

The chemical structure of the branched sugar chain polymer used in this study included alpha-linked disaccharide formed by 1,1-glycosidic bond between glucose units in an organic solvent-free water-developable branched sugar resist material derived from biomass (Fig. 1(a)). Water-developable sugar resist materials were synthesized by enzymatic decomposition, extraction, and purification of linear and branched sugar chain polymers [5,26,32]. The branched sugar chain polymers, which are derived from biomass, are also natural and eco-friendly compounds that are used for the first time in this study. These branched sugar chain polymers are expected to facilitate water development via formation of –OH groups and low film thickness shrinkage during EB irradiation due to the glucose ring structure [5]. The designed structures of side-chain groups in the resulting branched sugar chain polymers are EB curable acryloyl groups and –OH groups at a molar ratio of 80:20. The reactant of branched sugar chain polymers was refined in liquid such as water and alcohol for five times in sugar refinery process. The structure of the synthesized branched sugar chain polymers was confirmed by using attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy (Fig. 1(b)). The results match well with the ones previously reported in the literature [33,34]. The characteristic absorption maxima of –OH groups, –CH₂–, C=O stretching vibration, and –COC–, –CO– dominated by ring vibrations of carbohydrates in the sugar chain polymers is observed at 3600–3000 cm^{–1}, 3000–2700 cm^{–1}, approximately 1700 cm^{–1} and 1200–1050 cm^{–1}, respectively. In addition, a peak at around 1630 cm^{–1} corresponding to C=C stretching vibration of EB curable acryloyl groups in the sugar chain polymers is also seen. The sugar chain polymers had

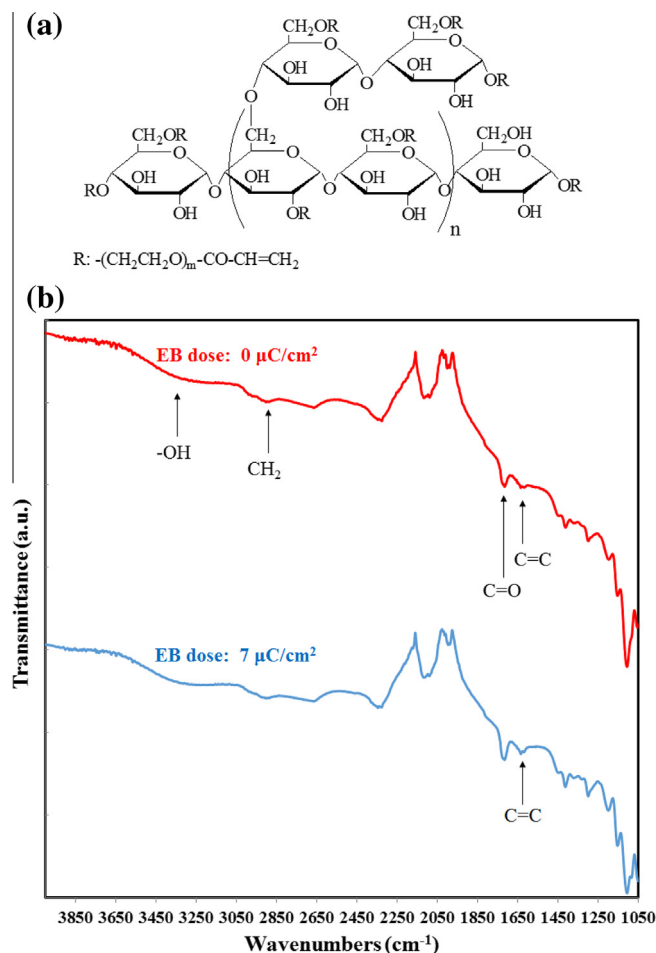


Fig. 1. Organic solvent-free water-developable branched sugar resist material. (a) Chemical structure of negative type of branched sugar chain polymer for water-developable resist material derived from biomass. (b) FT-IR transmission spectrum of branched sugar chain polymers with EB curable acryloyl groups.

the weight-average molecular weight of 95,000, and the range of polydispersity was 4.4 related to the standard polystyrene, in terms of the gel permeation chromatography (GPC) conditions described below. The calculated number-average degree of polymerization n in the branched sugar chain polymers was approximately 40.

2.2. Underlayers

The EB sensitivity, resolution limit, and etching properties of water-developable sugar resist materials was evaluated by using spin-on silicon-based hardmask layer and etching transfer layer in tri-layer processes of green EB lithography. In our previous study, we reported the hardmask layer and etching transfer layer were reported [25,35–38]. The hardmask material prepared in this study consists of a base polymer with EB curable methacrylate group (60 mol%), methyl group (15 mol%), cross-linking group (25 mol%), acid catalyst, and additives of coating and etching properties. Fig. 2 shows the chemical structure of the SiO₂-polymer in the hardmask material. The mixture of three SiO₂ precursors was stirred for 6 h to yield a clear and gel-free solution. In addition, the etching transfer layer consists of novolak polymer resin, hexamethoxymethylol melamine as the aminoplast crosslinker (Nihon Cytec Industries), and pyridinium *p*-toluenesulfonate (Tokyo Chemical Industry). The weight-average molecular weights of two base polymers in the hardmask layer and etching transfer

Download English Version:

<https://daneshyari.com/en/article/539476>

Download Persian Version:

<https://daneshyari.com/article/539476>

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