Microelectronic Engineering 182 (2017) 8–14

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Research paper

Local electric field direct writing – Electron-beam lithography and mechanism

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ARTICLE INFO

Article history:
Received 26 April 2017
Received in revised form 15 August 2017
Accepted 20 August 2017
Available online 24 August 2017

Keywords:
Nano-patterning
Composition modulation
Local electric field
STEM

ABSTRACT

Local electric field induced by a focused electron probe in silicate glass thin films is evaluated by the migration of cations. Extremely strong local electric fields can be obtained by the focused electron probe from a scanning transmission electron microscope. As a result, collective atomic displacements occur. This newly revised mechanism provides an efficient tool to write patterned nanostructures directly, and thus overcome the low efficiency of the conventional electron-beam lithography. Applying this technique to silicate glass thin films, as an example, a grid of rods of nanometer dimension can be efficiently produced by rapidly scanning a focused electron probe. This nanopatterning is achieved through swift phase separation in the sample, without any post-development processes. The controlled phase separation is induced by massive displacements of cations (glass modifiers) within the glass-former network, driven by the strong local electric fields. The electric field is induced by accumulated charge within the electron probed region, which is generated by the excitation of atomic electrons by the incident electron. Throughput is much improved compared to other scanning probe techniques. The half-pitch spatial resolution of nanostructure in this particular specimen is 2.5 nm.

1. Introduction

Conventional electron-beam lithography (EBL) creates patterns by scanning a focused electron beam on a surface covered with an electron-sensitive film (e-beam resist) to change the resists' solubility in certain solvents (developers), thereby leaving the resist intact only in the designated areas [1]. Direct-write EBL creates patterns directly on thin films using a focused electron beam without post-irradiation treatment [2]. EBL has the advantage of extremely high spatial resolution (e.g. ~10 nm) and the ability to direct write arbitrary nanostructures without a mask. However, either conventional or direct-write EBL is a sequential process that exposes a film of resist in a serial fashion. Therefore, the main shortcoming is its low efficiency, which largely limits its current applications to producing photomasks in optical lithography and producing small numbers of nanostructures for research purposes. To overcome this limitation, besides the projection EBL [3] and the use of multi-parallel beams [4], large efforts have also been made to search for suitable resist materials, which are not only able to produce desired nanostructures, but also extremely susceptible to electron beams and as a result, shorten the exposure time [5].

Electron-beam lithography is the result of electron-beam damage in resist materials. The success for exploring new resists relies on the understanding of damage mechanisms in the materials. Historically, the beam damage has been overwhelmingly interpreted as due to either knock-on displacement or radiolytic process [6–8]. Although two mechanisms operate differently in different materials, they all create Frenkel defects inside specimen and sputter (or desorb) atoms from surface. Therefore electron-beam lithography has been considered as the cause of defect accumulation or surface sputtering, and thus the lithography process is electron dose dependent [9]. Under this theoretical framework, the sensitivity of materials to electron beams are measured by the electron dose required to create an individual structure. For example, it was reported that drilling a hole of 5 nm in diameter in a 250 nm thick NaCl film required an exposure dose of 10^{-1} C/m^2 [10]. While drilling a similar hole in an 80 nm thick AlF_3 thin film required an exposure dose of 10^5 C/m^2, and this was accompanied by the formation of Al in areas adjacent to the irradiated areas [11]. Certainly, the low efficiency of electron-beam lithography is caused by this limitation of dose threshold required to form each individual nanostructure. The key operation conditions were then identified as beam energy and electron dose, and the latter was also used as an indication of the sensitivity of resist [9]. The required dose is in order of 1.0 C/m^2 in conventional EBL [5].

However this consideration is not fully accurate. Beam damage induced by high-current-density electron beam in a modern scanning transmission electron microscope (STEM) is not just limited to these mechanisms. In semiconductors and insulators, atom displacements

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http://dx.doi.org/10.1016/j.mee.2017.08.006
0167-9317/

are mainly caused by the mechanism of damage by induced electric field (DIEF) [12,13]. Two of the unique characteristics of this mechanism are (1) it is dose-rate dependent, and (2) the motion of the displaced atoms is in the manner of association and dissociation, which occurs when positively and negatively charged atoms moves toward opposite directions. In addition, it also governs the spatial resolution of EBL, which can be controlled by the strength of the induced electric field though manipulating beam current density in electron probe [14]. The electric field is induced by ejection of secondary and Auger electrons due to electronic excitations and ionizations [12–16]. If the induced electric field is strong enough to overcome the activation energy for ion migration, the atoms of the same kind may be displaced collectively [12,13]. By this means a type of swarm behavior causes the same species of atoms to move together coherently. Although the theory of this mechanism was not given until in the recent studies [12,13], the experimental phenomena have been widely observed for several decades [17–24]. Due to the same reason, the DIEF mechanism has not been seriously considered in EBL. In the previous EBL studies, hole-drillings have been related to the possible involvement of electric field [15,18], but it was not seriously considered until in the recent discussion of spatial resolution limitation of EBL [14].

Although the mechanism of DIEF has been applied to understanding the spatial resolution of EBL [14], the detailed processed and applications have not yet been introduced. In this work, we demonstrate a revived technique for EBL that uses the highly localized electric field induced by a focused electron probe in a STEM. Patterning nanostructures using this technique is achieved through manipulating phase separation, which is triggered by the electric field and occurs rapidly. This electric-field driven lithography is determined by the dose rate (current density of electron beam) rather than the dose. Therefore, the conventional understanding of both efficiency and spatial resolution of electron-beam lithography needs to be updated. It should be pointed out that this technique is currently limited to prototyping of research devices.

For convenience, here we use thin films of silicate glasses as examples for demonstration. Micro- and nanolithography in transparent materials are promising approaches for introducing new functionalities into glasses in electronic applications and nanostructures. Previously, most studies were focused on the use of high-power ultra-short (e.g. femtoseconds) pulsed lasers to modify glasses [25–28], since the focused sub-bandgap wavelength fs-laser pulses can efficiently and precisely deposit energy into a micron-sized volume, and induce localized structural and chemical changes inside the bulk, or on the surface [29]. Unfortunately, the spatial resolution of this technique is limited by the wavelength of laser beam, and it is impossible to construct structures on a nanometer scale. In STEM, beam electrons have much shorter wavelength (e.g. wavelength $\lambda = 2.5$ pm for a 200 keV electron). Although it is difficult to modify bulk glass due to its short penetration distance, electron beam is ideal for nano engineering either self-supported or supported thin film glasses with thicknesses of less than about a micron. Since the physical and optical properties of glass depend on its composition [30], new functionalities of glass can thus be achieved without further chemical etching processes. It should be pointed out that this lithographic technique can be also applied to other materials.

2. Experimental

Silicate glass used in this study has nominal composition of $25CaO\text{-}75SiO_2$ (mol%). The glass was made by the conventional melt-and-quench method. The TEM specimens were prepared using a standard wedge polish technique from a Multi-prep system (Allied High Tech.). The polished specimens were Ar-ion milled (1.5 kV) at liquid nitrogen temperature for 5 min using a Gatan Precision Ion Polishing System (PIPS). A 200 kV JOEL-2010F TEM/STEM was used for both nanopatterning and characterization. In STEM mode, a high current density probe (10 pA, 0.2–0.5 nm in diameter) was used for nanopatterning, and a low current density probe (1.0 pA, 0.5 nm in diameter) was used for characterization. The microanalysis of the nanostructures produced was carried out by electron energy-loss spectroscopy (EELS). EELS spectra were collected using a Gatan Enfina electron spectrometer with energy resolution of 1.0 eV. The acquisition time was 10^{-6} s for each spectrum. Both imaging and electron diffraction were also carried out using TEM mode.

3. Results

Fig. 1(a) shows a TEM phase-contrast bright-field image of a grating pattern produced by rastering a focused electron probe (~0.2 nm in diameter) across the glass. Considering that the TEM image is a 2-*d* projection of a 3-*d* structure along the beam direction (defined as the z-axis here), each bright dot in Fig. 1(a) represents a "nano-rod", whose length is the thickness of the specimen (detailed later). As shown in an enlarged image (Fig. 1b), the diameter of the nano-rod estimated from the phase-contrast image is about 2.5 nm. Each nano-rod was produced by exposure to the focused electron probe for 0.005 s, and the arrays of nano-rods were created by rastering electron probe along the x- and y-direction subsequently (as indicated in Fig. 1a and b) over an area of about 0.36 μm by 0.31 μm. The scan step was 7.4 nm along x-direction and 6.2 nm along y-direction. To produce a 50×50 nano-rod-array, the total exposure time was only about 7.5 s. It should be pointed out that although the exposure for each nano-rod was approximately in order of 100 C/m^2, this is not the sensitivity of the resist, which is discussed later.

Modifications of the structure and composition of these nano-rods can be examined by small-angle electron diffraction, since the spacing between the nano-rods is fairly large. Confined by a selected-area aperture, the small-angle electron diffraction pattern from the array of nano-rods in Fig. 1a was obtained, as shown in Fig. 1c. For amorphous materials, the electron diffraction pattern consists of blurred rings, and the diameter of the first ring is related to the average bond length of the material. In silicate glasses, the first ring usually occurs between 5–10 nm^{-1} in the diffraction pattern, which is way out of the range in Fig. 1c. The diffraction spots observed in Fig. 1c are formed by the diffracted beams from the periodically arranged nano-rods. As schematically shown in Fig. 2, the arrays can be considered as a 2-*d* pseudo-crystal of nano-rods, with lattice parameters of D_x and D_y, respectively. The potential seen by the incident electron can be approximately expressed as $V = V_0 + \Delta V$, in which V_0 is the average potential of amorphous matrix and ΔV is the perturbation potential due to the nano-rods. Since the nano-rods are periodically arranged, ΔV can be expressed according as a Fourier series as,

$$\Delta V(\mathbf{r}) = \sum_{g} \Delta V_g \exp(-2\pi i \mathbf{g} \cdot \mathbf{r}) \tag{1}$$

in which $\mathbf{g}$ are 2-*d* reciprocal vectors defined by the 2-*d* pseudo-lattice of nano-rods, with units of $g_x = 1/D_x$ and $g_y = 1/D_y$. According to electron diffraction theory [31], ΔV_g is related to the periodic structure of nano-rods via relation:

$$\Delta V_g = \frac{1}{V_C} \sum_{j} \Delta f_j \exp(-2\pi i \mathbf{g} \cdot \mathbf{r}_j) \tag{2}$$

The sum is over all the atoms in one nano-rod, which has volume of $V_c = \pi w^2 t/4$ (Fig. 2). Since the nano-rods are embedded in the glass matrix, it is reasonable to assume that $\Delta f_j = f_j - \overline{f}$, in which f_j is the electron scattering factor of the *j*th atom and $\overline{f}$ is the average electron scattering factor of the glass matrix. Therefore, Δf_j will only cause significant electron diffraction if the composition of nano-rod is very different from the glass matrix.