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APSUSC-27747; No. of Pages 12
ARTICLE IN PRESS
Applied Surface Science xxx (2014) xxx–xxx
Contents lists available at ScienceDirect
Applied Surface Science
journal homepage: www.elsevier.com/locate/apsusc

Resist materials for proton beam writing: A review

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ARTICLE INFO

Article history:
Received 31 December 2013
Received in revised form 17 April 2014
Accepted 18 April 2014
Available online xxx

Keywords:
Proton beam writing
Resist materials
Ni electroplating

ABSTRACT

Proton beam writing (PBW) is a lithographic technique that has been developed since the mid 1990s, initially in Singapore followed by several groups around the world. MeV protons while penetrating materials will maintain a practically straight path. During the continued slowing down of a proton in material it will mainly interact with substrate electrons and transfer a small amount of energy to each electron, the induced secondary electrons will modify the molecular structure of resist within a few nanometers around the proton track. The recent demonstration of high aspect ratio sub 20 nm lithography in HSQ shows the potential of PBW. To explore the full capabilities of PBW, the understanding of the interaction of fast protons with different resist materials is important.

Here we give an update of the growing number of resist materials that have been evaluated for PBW. In particular we evaluate the exposure and development strategies for the most promising resist materials like PMMA, HSQ, SU-8 and AR-P and compare their characteristics with respect to properties such as contrast and sensitivity. Besides an updated literature survey we also present new findings on AR-P and PMGI resists. Since PBW is a direct write technology it is important to look for fast ways to replicate micro and nanostructures. In this respect we will discuss the suitability and performance of several resists for Ni electroplating for mold fabrication in nano imprint technologies. We will summarize with an overview of proton resist characteristics like sensitivity, contrast, aspect ratio and suitability for electroplating.

1. Introduction

Proton beams have been used in masked lithography since 1979 [1]. In early experiments Adesida [2] and Brenner et al. [3] used low energy (200 keV) and high energy (8 MeV) proton beams respectively for masked irradiation of PMMA resist materials. In this early work Adesida produced rather rough sub-100 nm features, whereas Brenner et al. produced very high aspect ratio structures featuring lateral dimensions of tens of microns. It took a long time before protons were used more seriously in lithographic experiments. More recently proton beam writing (PBW) was introduced as a direct-write lithography process developed at the Centre for Ion Beam Applications (CIBA), Department of Physics, National University of Singapore [4–6]. The proton beam writing technique relies on a precise beam scanning and control system that offers a simple yet flexible interface for the fabrication and design of micro- and nanostructures using focused protons with a spot size down to 20 nm [7].

In proton structuring of resist materials there are two main modes of exposure. The choice between masked- or focused beam exposure depends on the nature of the application. In both cases resist characteristics like sensitivity, contrast and nature of the resist (positive or negative tone) are crucial for the success of the lithographic task at hand. In the case of metallic mold fabrication the resist needs to be easily removable after Ni electroplating, limiting the choice of resist materials. Equally important is the fact that protons travel in a relatively straight path and the secondary electrons produced have limited range [8,9] allowing unique structuring of 3D nanostructures with high aspect ratios (height/width).

1.1. Exposure strategies

To facilitate high aspect ratio 3D nanostructuring of resist material, PBW using a focused beam has shown the most promising results. At CIBA Ionscan software is used to pattern resist materials in PBW experiments. The Ionscan software suite is comprised of sub programs to control beam scanning, beam blanking, stage movement and file conversion. The first version was developed using *LabVIEW* [10]. Many new features have since been added into the software, e.g. the ability to perform combined stage and beam scanning, resist calibration, dose calculation, scan parameters settings

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http://dx.doi.org/10.1016/j.apsusc.2014.04.147
0169-4332/

Please cite this article in press as: J.A. van Kan, et al., Resist materials for proton beam writing: A review, Appl. Surf. Sci. (2014), http://dx.doi.org/10.1016/j.apsusc.2014.04.147

and automated serial writing [11]. Every exposure pattern is digitized with a resolution up to 16 bit with a minimum pixel dwell time of 1 μs/pixel. The maximum beam scan area depends on the beamline used and is either 500 μm × 500 μm [5] or 100 μm × 100 μm [7] for the 1st and 2nd generation PBW systems respectively. In PBW experiments it is important to have a stable and reliable exposure system, and especially the proton source brightness and choice of the proton beam energy are important factors in achieving high quality high aspect ratio micro and nanostructures.

Several groups have used collimated proton beams for resist lithography with MeV protons. Tuteleers et al. [12,13] have introduced high energy (8–16.5 MeV) masked exposures for the production of optical components made from PMMA. At CIBA ion projection lithography of Si using molecular proton beams has been introduced by Mangaiyarkarasi et al. [14] to fabricate a variety of optical and photonic components in Si over wafer areas of several square centimetres. This process is based on a projection system involving a megavolt accelerator and a quadrupole lens system to project a uniform distribution of MeV ions over a wafer surface, which is coated with a multilevel mask. The features in the mask determine the resolution of the process. In conjunction with electrochemical anodization, this enables the rapid production of waveguides and optical microcavities for applications in high-definition reflective displays and optical communications.

As an alternative approach Puttaraksa et al. [15] introduced a programmable proximity aperture lithography (PPAL) technique. Using this PPAL technique they have made a large area microfluidic chip with complex components having large and small (1–500 μm) patterned elements on PMMA. After bonding the PMMA chips were used in fluidic environment. In this technique, a rectangular or square exposed area on the sample is adjustable and determined by two computer-controlled L-shaped aperture blades. A LABVIEW™ program controls the opening aperture area, the exposed sample position and the beam blanking. Complex structures can be built up by connecting several pattern elements with control up to 100 nm translational steps with 2 μm accuracy in bidirectional setting and 4 μm accuracy in absolute position. In the case of 3 MeV $^4He^{2+}$ ions, the exposure time used is approximately 45 s per pattern element corresponding to an ion fluence of 2.5×10^{13} ions/cm^2.

1.2. Technological challenges and proton interaction with resist

To achieve features below 10 nm using PBW several technological challenges need to be met. We have identified three main requirements:

Firstly: A lens system must be able to focus proton beams down to nm sized dimensions. The lens system developed in CIBA [7,16] is expected to be able to cross the 10 nm barrier.

Secondly: The proton source brightness in available PBW systems is currently very low and needs to be improved in order for PBW to become a viable contender in nanolithography. Novel ion source ideas are being evaluated at the moment [17].

Thirdly: A suitable resist material and development procedure need to be employed to realize sub 10 nm resist features. To explore the full micro- and nano-fabricating capabilities of protons in lithography, and PBW in particular it is important to understand the interaction of MeV protons with resist materials. MeV protons generate secondary electrons and, as in many lithographic processes these electrons modify the molecular structure of the resist. The energies of the proton induced secondary electrons are relatively low, and most have energies of a few tens of eVs. In the case of chain scissioning of polymethyl methacrylate (PMMA), which acts as a positive resist under proton exposure, a minimum energy of ~3.4 eV is required to break such bonds. In the case of hydrogen silsesquioxane (HSQ), 4.08 and 8.95 eV are needed to break the Si–H and Si–O bonds respectively and form a crosslinked network insoluble to developer, rendering it a negative resist. Therefore proton induced secondary electrons only modify resist material within several nano meters of the proton track and are thus ideal for resist lithography. Since protons mainly interact with the substrate electrons the path of the proton beam is very straight, resulting in smooth and well defined resist structures with practically no proximity effects, except if a "thick" resist layer is used which is comparable in thickness to the range of the proton beam in that resist material, in which case the protons will undergo increased nuclear scattering at the end of range. Calculations show that this leads to a beam spread of only a few nano meters. The exact value depends on beam energy and resist material [8]. When calculating the energy deposition due to the proton induced secondary electrons [18] it is clear that PBW has the potential to make structures below 10 nm in width in layers of at least 500 nm thickness.

In this review we will discuss achievements related to resist exposure using MeV protons. We will discuss most of the positive and negative resist materials which are used in proton exposure. We will also discuss nuclear interactions that lead to materials modification using proton beams. In this review we will only select a few materials, presenting a flavour of some of the possibilities.

2. Positive resist

2.1. PMMA

Poly(methyl methacrylate) (PMMA or Plexiglas) is a popular resist, utilized in many different lithographic processes. Primary advantages of PMMA include its simple structure, non toxic nature of the solvent (anisole), several possible dilutions allowing a wide range of resist thickness, non sensitivity to white light ($\lambda > 250$ nm), high resolution, no shelf life issues, no processing delay effects, and it can be easily removed after Ni electroplating, unless the resist has been crosslinked. With these flexible properties PMMA is a powerful resist material, which has great potential in Ni mold fabrication.

PMMA was one of the primary resists tested during the earlier study of PBW at CIBA [4]. Through these studies superior patterning capabilities (sub-100 nm) of PBW on PMMA have become well-known. Results show that trenches as small as 65 nm [19] and 50 nm narrow walls with an aspect ratio of 7 can be written in PMMA [5]. Fig. 1 shows an SEM image of parallel lines written in a 350 nm thick PMMA layer (7 aspect ratio). The structure was written with a focused 2 MeV proton beam. The photo indicates a wall width of 50 nm, reproduced with permission from [5].

CIBA has also achieved superior results for the Ni electroplating process with proton beam patterned primary PMMA molds. Ansari et al. [20] have reported a way of fabricating high-quality void-free high-aspect-ratio Ni stamps having ridges of 100 nm width and 2 μm depth. Nanoindentation and atomic force microscopy measurements of the nickel surfaces of the fabricated stamp show a hardness and side-wall roughness of 5 GPa and 7 nm, respectively. The fabricated 100 nm 3D stamps have been used to transfer test patterns into PMMA films, spin coated onto a Si substrate. PBW coupled with electroplating offers a prospective process for the fabrication of high quality metallic 3D nanostamps. Fig. 2a shows a low magnification SEM image of a Ni stamp fabricated using PBW and Ni electroplating. The stamp is a test pattern featuring two raised platforms connected by several 100 nm wide × 2 μm depth × 30 μm length high aspect ratio ridges. Fig. 2b shows an SEM image showing three of the connecting 100 nm Ni stamp ridges, and Fig. 2c shows a high magnification picture of one Ni ridge, exhibiting vertical sidewalls, and a smooth surface (7 nm rms), reproduced with permission from [20].

Uchiya et al. [21] have reported patterning of high aspect ratio structures in 5 μm thick PMMA and making use of them as a