Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Microelectronic Engineering 83 (2006) 767–770
MICROELECTRONIC ENGINEERING
www.elsevier.com/locate/mee

Three dimensional HSQ structures formed using multiple low energy electron beam lithography

Euan J. Boyd *, Richard J. Blaikie

MacDiarmid Institute for Advanced Materials and Nanotechnology, Department of Electrical and Computer Engineering, University of Canterbury, Private Bag 4800, Christchurch 8020, New Zealand

Available online 3 March 2006

Abstract

A method is presented for the fabrication of three-dimensional (3D) structures formed in hydrogen silsequioxane (HSQ) by a process of multiple low energy electron beam exposures with a single development step. Structures have been produced consisting of multiple layers of dielectric rods with widths and heights of 150 nm and a separation of 1μm in the horizontal plane and 360 nm in the vertical direction.

Keywords: HSQ; Electron beam lithography; Low energy; Three-dimensional structures

1. Introduction

Hydrogen silsequioxane (HSQ) is an inorganic three-dimensional polymer material. It is available commercially from Dow Corning under the name Fox-12©. In its uncured form HSQ is combination of a caged oligomer with a general formula of $(HSiO_{3/2})_{2n}$ and a larger network structure. Curing leads to a formation of a three dimensional structure by the cage structures forming networks either by cross-linking by condensation of Si-OH groups to Si-O-Si bonds or the cage structures opening and reforming in a network structure [1]. It is this change from a spinnable polymer to a robust low-k dielectric that has made HSQ promising as a material for planarisation [2,3]. The curing process can be performed either by thermal annealing or electron exposure. It was originally found by Namastu that the change in structure and hence solubility with electron exposure allows HSQ to be used as a negative tone electron beam resist [4]. It is has been since shown to be a highly successful electron beam resist, capable of producing very high resolution patterns [5], with low line edge roughness [4]. The structure of the exposed material is similar to silicon dioxide and thus it has a high dry etch resistance and is mechanically stable. The mechanical stability of exposed HSQ is used in this work.

Tanenbum et al. demonstrated suspended HSQ structures using a dual exposure technique [6]. They used the shallow penetration of low energy electrons to define thin HSQ wires suspended between two large supports. In this work this low energy technique is extended from writing single layers of HSQ to multiple layers which are exposed sequentially and developed out in a single step.

2. Process development

Fig. 1 illustrates the process flow of the multiple layer, multiple exposure technique. A layer of HSQ is spun on the substrate and the surface of this layer is then patterned using a low energy electron beam. The depth of this pattern can be controlled by varying the electron energy. A second layer of HSQ is then spun on top and then patterned in the same way as the first layer. Support structures are written using an electron energy high enough to penetrate the entire resist stack. This connects the two low energy layers with the substrate. The sample is then developed out revealing a 3D pattern of two layers of suspended filaments supported by the high-energy structures.

* Corresponding author. Tel.: +64 3 364 3274; fax: +64 3 364 2761.
E-mail address: euan.boyd@canterbury.ac.nz (E.J. Boyd).

0167-9317/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mee.2006.01.253

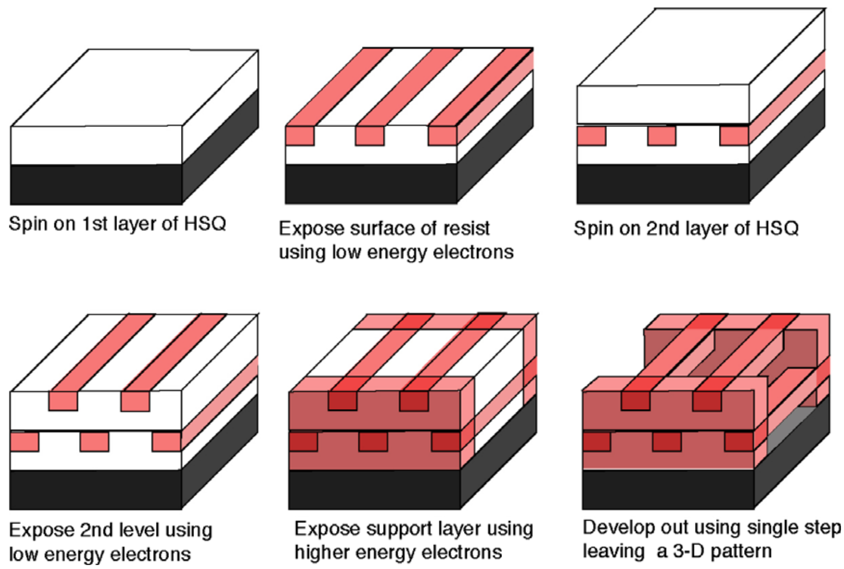

Fig. 1. Illustration of process flow of the multiple layer, multiple exposure technique.

2.1. *Penetration depth of low energy electrons*

The tool that is used in this work is a Raith 150 EBL system; this is based on a LEO 1500 series scanning electron microscope with a thermal field-emission source and a Gemini column. The system is capable of a range of beam acceleration voltages of between 200 eV and 30 keV.

As the accelerating voltage of the column is reduced the penetration depth of the electrons within the resist is reduced. Monte Carlo simulations of the path of electrons subject to various accelerating voltages into a 400 nm thick layer of HSQ were conducted using CASINO [7]. The paths of electrons with various accelerating voltages are shown in Fig. 2(a). It is seen that the range of the 1 kV elec-

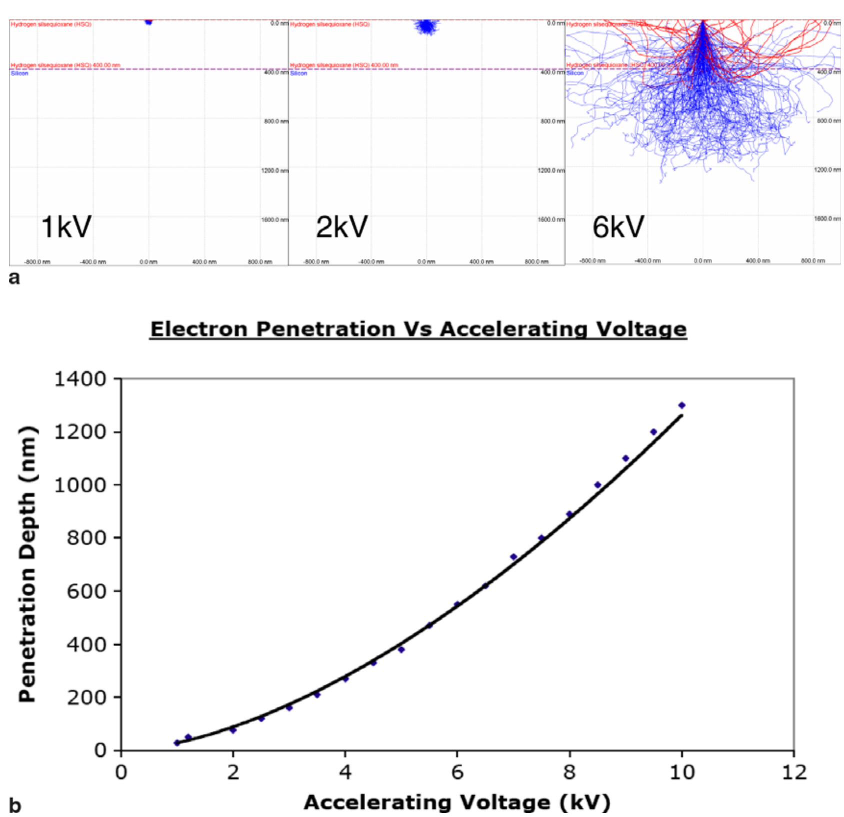

Fig. 2. (a) Plots of electron paths for 1, 2, and 6 kV accelerating voltages simulated with CASINO. (b) Plot of electron penetration depth versus accelerating voltage.

trons is very small, around 50 nm, and as the voltage is increased to 6 kV the electrons are able to pass through the 400 nm HSQ layer and into the substrate. At 100 kV the electrons pass through the HSQ and deep into the substrate with little interaction. Fig. 2(b) shows the penetration depth as a function of accelerating voltage.

It is therefore possible to use the accelerating voltage of the incident electrons to control the depth of the written pattern in addition to the width and length control that is available with traditional electron beam lithography. This has been verified experimentally. A test structure was fabricated by writing a number of low energy single pixel lines written at 900 pC/cm between support structures with a 10 μm gap. Over this large gap, the filaments collapse onto the substrate and the height can be measured using atomic force microscopy (AFM). Fig. 3 shows the thicknesses of filaments written with a dose of 900 pA/cm using accelerating voltages of 2, 3 and 6 kV, as well as the dependence of thickness and width for 2 keV exposures. The widths were measured by SEM and the thickness by AFM. The energy dependence of the exposures is clearly seen in Fig. 3(a), it is seen that the filaments are roughly square shaped and vary little across the dose range as shown in Fig. 3(b).

2.2. High contrast development

Due to the writing of multiple layers the structure has a high exposure density. Low energy electron beam exposure has the advantage of having a low scattering length that minimizes proximity effects [8]. However, the standard development of 60 s in AZ300MIF (2.38% tetra-methyl ammonium hydroxide) originally used to produce less closely packed single layered structures lacked the contrast necessary for multilayered structures. A number of development strategies were tested to increase the contrast including increasing the strength of developer and the post development bake suggested by Tanenbum et al. [6]. The post development bake worked the best for our structures. It was however necessary to reduce the baking temperature from 250 °C to 180 °C and increase the development time from two minutes to five minutes to fully clear out the unexposed resist below the filaments.

2.3. Spinning multiple layers

An issue with any process that involves application of multiple layers of resist is to ensure that the spinning of subsequent layers of resist does not affect the previous layer. The general method of applying HSQ is to spin coat the wafer; this allows thick uniform layers to be applied, however the solvents from the liquid resist can dissolve the initial layers changing the overall thickness of the two layer film. This effect has even more importance for this work as the initial layer that has already been exposed is on the surface any mass flow may deform the exposed pattern. The thinning of resists during spinning is caused by two mechanisms, fluid flow and evaporation. In the first stage, the fluid is driven off the sample limited by the viscosity of the film. This radial flow quickly reduces because the film gets very thin and the viscosity of the film increases due to evaporation. In the second stage, the fluid flow stage has effectively halted and the thinning of the film occurs largely due to evaporation.

In order to minimize the re-dissolving and fluid flow of the underlying layers of resist the time that the solvent is in contact with the pre-spun layer was minimized. This was achieved by applying the resist to the samples when spinning at 4000 rpm. This method works for small samples but may have to be modified if larger samples were used. The transfer from the fluid flow to evaporation stage was encouraged by increasing the airflow over the sample during spinning. This was found to increase the uniformity of the resist covering the exposed pattern.

2.4. Topographical markers

This technique relies on the ability to align multiple low energy exposures on different layer, however, the low energy nature of the exposures precludes the use of traditional gold alignment marks on the substrate. Topographical markers were therefore used in this work. These are

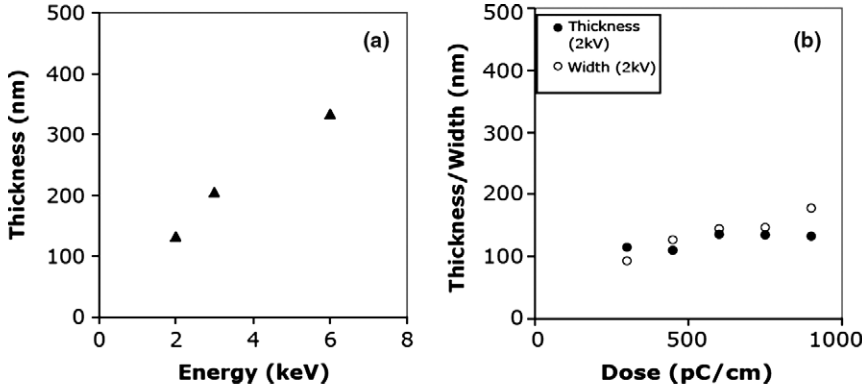

Fig. 3. (a) Thickness of HSQ filaments versus electron energy. (b) Thickness and Width of 2 kV filament versus dose.

typically formed by etching deep pits into the surface of the silicon wafer. The design of the pattern must be considered, so that the point chosen to align to remains visible even when thick layers of resist are applied. The structure that was used was defined by photolithography and consisted of four $50 \times 50 \mu m$ squares arranged to leave a cross in the centre with a line width of 20 μm. The pattern was transferred into SiN_x to create a mask for the KOH etch. The markers were etched to a depth of around 50 μm. The size of the markers allows multiple layers of resist to be spun without filling, and the small centre of the cross can still be picked up accurately in the SEM.

3. Fabrication

Using the methods discussed above a three-dimensional structure was fabricated to demonstrate this multilayer, multiple exposure technique. The structure consisted of two layers of gratings with a period of 1 μm. The structures span a 4 μm gap between support structures. The filament structures were written using an accelerating voltage of 2 kV and a dose of 600 pC/cm to give a cross section of 135×145 nm, less than half the thickness of a HSQ layer spun at 4000 rpm. The accelerating voltage of the support structures has to be chosen carefully; the majority of electrons must penetrate the full thickness of the two HSQ layers but not scatter too much at the surface of the silicon, which can lead to problems developing out under the lower filaments. An accelerating voltage of 7 kV was used with a dose of 800 pC/cm.

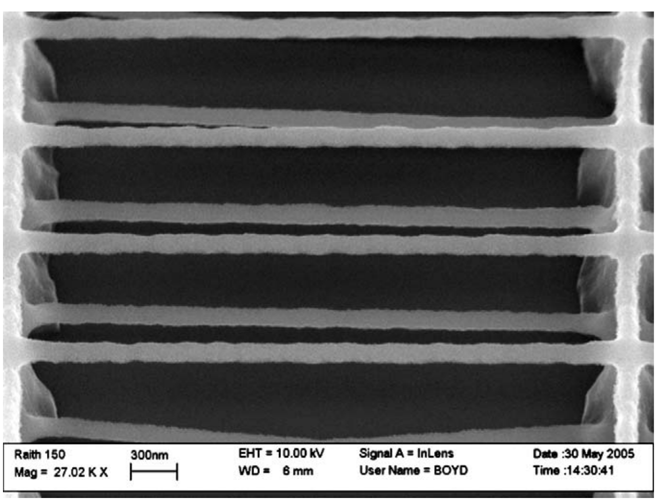

Fig. 4. SEM Micrograph of a two layer grating structure fabricated using multiple low energy exposures. The sample is tilted at an angle of 40° demonstrating that the gratings are fully suspended.

The resultant structure is shown in Fig. 4. The sample has been tilted by 40° showing that the filaments are fully suspended from the support structures and are separated from each other, both laterally and vertically. The dimensions of the upper and lower filaments are around 120 nm as was found for the single layer experiment described earlier.

4. Conclusions

This work has demonstrated the possibility of fabricating multilayer three-dimensional structures by a technique of low energy electron beam lithography into HSQ. Further refinements of this technique such as improved alignment and resist deposition will allow more complex structures to be fabricated such as three-dimensional photonic crystal structures.

Acknowledgements

The Authors thank Neil Andrews from the School of Biological Sciences for his assistance in imaging the three-dimensional structures.

References

[1] C.-C. Yang, W.C. Chen, J. Mater. Chem. 12 (2002) 1139.
[2] M.J. Loboda, G.A. Toskey, Solid State Technol. 41 (1998) 99.
[3] M. Qi et al., Nature 428 (2004) 538.
[4] H. Namatsu et al., Microelectron. Eng. 41/41 (1998) 331.
[5] K.A. Lister et al., Microelectron. Eng. 73/74 (2004) 319.
[6] D.M. Tanenbaum et al., J. Vac. Sci. Technol. B 19 (6) (2001) 2829.
[7] CASINO Website, Available from: http://www.gel.usherbrooke.ca/casino/index.html.
[8] A. Olkhovets, H.G. Craighead, J. Vac. Sci. Technol. B 17 (4) (1999) 1366.