Electron Beam Lithography of Bulk Zinc Oxide Wafers using a Polythiophene-based Charge Dissipation Layer

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***Abstract*—The ability of thin conductive polythiophene layers to dissipate electrons in electron-beam lithography process on ZnO is presented for the first time. Quick and inexpensive processing method is shown for an EBL exposure of dense and high-resolution patterns in hydrogen silsesquioxane (HSQ) negative-tone resist deposited on bulk ZnO sample.**

Keywords-electron-beam lithography; zinc oxide; hydrogen silsesquioxane (HSQ); conductive polymer; PSS:PEDOT; photonic crystal

I. INTRODUCTION

Zinc oxide (ZnO) is a wide bandgap semiconductor that is attracting much attention these days due to its potential for fabricating blue light emitting devices. This II-VI oxide semiconductor has about the same bandgap (~ 3.4 eV) as gallium nitride (GaN) which is now the standard material for making short wavelength light emitting diodes and laser diodes. ZnO has a number of advantages over GaN when it comes to making similar devices. These include higher exciton binding energy and availability of bulk substrates. On the other hand, processing of ZnO is still developing and research groups are working on a number of areas that still require significant work [1, 2]. Electron-beam lithography pattering of ZnO is usually performed with a thin conducting metal layer (e.g., aluminium) deposited on top of the e-beam resist, due to electrostatic charging problem encountered with this material. Removal of Al layer after the exposure process is difficult because ZnO, being an amphoteric oxide, is easily attacked by both acids and bases used for this purpose. In this paper we describe the successful use of electrically conducting polymer – polythiophene – as a charge dissipation material for ZnO patterning through e-beam lithography.

II. EXPERIMENTAL DETAILS

We used commercially available 2.5% water-based dispersion of Poly(2,3-dihydrothieno-1,4-dioxin)-poly(styrenesulfonate), i.e. PEDOT:PSS from Sigma-Aldrich. Four point measurements of 6 μm thick films give surface resistivity values of 1200 Ω/square which falls to values below 500 Ω/square when films are made 20 μm thick. This later value corresponds to conductivity values in the range of 140-150 S/cm. The high electrical conductivity and good oxidation resistance of these polymer films make them suitable for electromagnetic shielding and noise suppression applications.

The bulk zinc oxide wafers, grown by a hydrothermal process, were cleaned by a wet chemical cleaning routine, followed by two hours of sample pre-bake on a hot plate. For trial exposures, 670 nm of undiluted hydrogen silsesquioxane (HSQ) negative e-beam resist was deposited on the samples by spin-coating at 2000 rpm for 60 seconds. Successful usage of HSQ as both the electron-beam resist and hard-mask for dry etching process was reported earlier for the fabrication of high-aspect ratio features in InP-based materials, with the use of chlorine-based inductively coupled plasma (ICP) dry etching [3, 4]. For comparison purposes three different samples were prepared: one sample with a single HSQ resist layer without any conductive film and two other samples with additional electron dissipation layers: one with an Al layer and one with a PEDOT:PSS layer. The conductive Al layer (40-nm-thick) was deposited with an electron-beam evaporator on the top of HSQ resist. For the last sample, PEDOT:PSS was deposited on HSQ surface by spin-coating at 5000 rpm for 60 seconds. This resulted in a conductive polymer layer with a thickness of 100 nm. Test features were defined directly in the HSQ mask layer using electron-beam lithography with a Vistec VB6 UHR machine operating at 100 kV. Software-based proximity correction was applied to the design prior to the exposure process in order to minimize electron backscattering effects on dense patterns. The fabricated patterns included a 50 μm × 10 μm area of pattern W1 (one row of holes removed) and W3 (three rows of holes removed) photonic crystal waveguide structures with a triangular lattice of holes (periodicity of 550 nm, designed hole diameter of 440 nm, radius to lattice period r/a ratio of 0.4). For each sample 25 different electron beam doses were investigated, with exposure doses varying in the range of 300 μC/cm^2 - 700 μC/cm^2. After exposure and prior to sample development, the polymer conductive layer was removed by using a warm bath of deionized water (55°C) for 2 hours. Samples were further investigated with a scanning

electron microscope, while image processing and analysis were performed with the use of ImageJ software [5].

III. Results and Discussion

The results of SEM micrograph analysis for each investigated case are presented in Fig. 1, while micrographs of PhC structures exposed with two different doses (333 and 474 μC/cm^2) are shown in Fig. 2. It is seen that the diameter of a single hole located within a photonic crystal lattice decreased with the increase of exposure dose, as expected for a negative-tone resist. For HSQ resist exposed without any electron dissipation layer (Fig. 1, square points), a steep dependence of hole dimensions against applied doses is noticed with a large scattering of experimental points. Additionally, severe overexposure of the dense pattern was observed for the majority of doses used in the experiment, starting from a dose of ~ 390 μC/cm^2. For a lower applied dose, i.e. 333 μC/cm^2, holes are slightly underexposed and not very sharply defined (Fig. 2a, SEM picture on the left). Usage of a higher dose (474 μC/cm^2) resulted in properly defined features on the edges of an array, while the middle part of the PhC lattice exhibited signs of strong proximity effect (Fig. 2a, micrograph on the right).

For a standard metal layer and conductive polymer layer, more gentle and gradual pattern variations were achieved. Sharply defined holes of similar size were obtained within highly uniform photonic crystal lattices, both for Al and PEDOT:PSS layers, as shown in Figs. 2b and 2c. For a wide range of doses, performance curves of these two conducting materials were highly comparable. Additionally, for lower exposure doses better definition of holes was noticed when 100-nm-thick PEDOT:PSS was used as the charge dissipation layer. The conductive polymer layer assured appropriate shape preservation within the whole range of investigated doses. While for Al, underexposed patterns with insufficient hole definition were observed for doses < 345 μC/cm^2 (Fig. 2b, on the left).

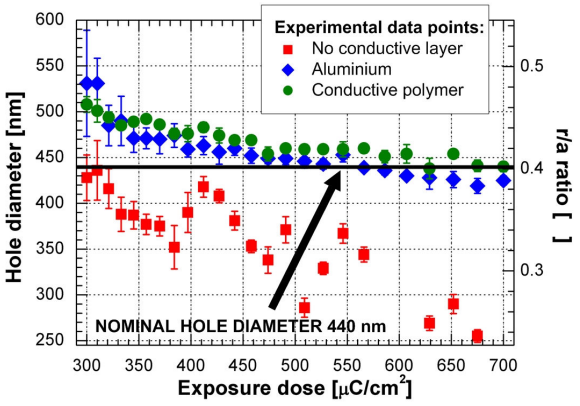

Figure 1. Experimental values of hole diameter and corresponding radius to lattice period (r/a) ratio against electron-beam lithography exposure dose, for three different exposure conditons: without any conductive layer (square points), with 40-nm-thick Al layer used (rhombus points) and 100-nm-thick PEDOT:PSS layer used (circle points).

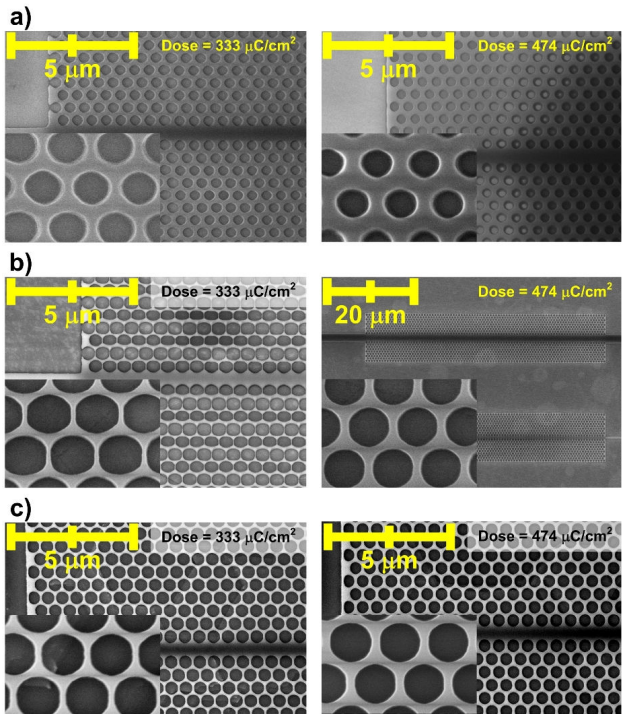

Figure 2. SEM micrographs of overall photonic crystal lattice and hole shape evolution in HSQ resist for doses of 333 and 474 μC/cm^2 and different exposure conditons: a) exposure without any conductive layer; b) 40-nm-thick Al layer used; c) 100-nm-thick PEDOT:PSS conductive polymer layer used.

IV. Conclusions

The excellent performance of PEDOT:PSS conductive polymer to dissipate charge in electron-beam lithography, in comparison with typically used metal layers, e.g. aluminium, was demonstrated experimentally. The new approach provides the ability to make ZnO sample processing much simpler, quicker and less expensive, but it may also be extended to EBL exposures of many other semiconductor/dielectric materials as well as to their observations in scanning electron microscopes.

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