Electron Dose Reduction Through Improved Adhesion by Cationic Organic Material with HSQ Resist on an InGaAs Multilayer System on GaAs Substrate

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1. ABSTRACT

This paper presents the findings of a cationic surface active agent used to promote adhesion on an InGaAs multilayer system on GaAs. The improved adhesion of the HSQ resist allowed the electron exposure dose to be reduced by a factor of four, and enabled the production of features sizes down to 30nm. Moreover, the process latitude is greatly increased for both small and large lithographic features.

2. MOTIVATION AND APPLICATION

In order to determine the properties and the resolving power of a Near Field Scanning Optical Microscope (NSOM), a suitable test structure made of an optoelectronic semiconductor material was needed. The required novel device was manufactured using a combination of electron beam lithography (EBL) and reactive ion etching (RIE). The semiconducting material selected was a multilayer InGaAs system on GaAs substrate. Hydrogen silsesquioxane (HSQ) was used as EBL negative resist. HSQ has attracted much attention and use in recent years due to its high resolution at the nanometer scale [1]. The high mass density of the InGaAs / GaAs substrate leads to strong electron back-scattering and consequently a strong e-Beam proximity effect. In addition to electron scattering, HSQ shows strong process effects which needed to be included in the correction [2]. In this work we see that on top of proximity and process effects the resolution of small features has been limited by adhesion problems of HSQ resist during development. In order to resolve feature sizes down to 30nm, the EBL process had to be optimized for proximity effects (PEC) as well as for resist adhesion during development.

3. EXPERIMENTAL

This paper describes the manufacturing of arrays of nano columns in an InGaAs multilayer system on GaAs. The exposures were performed using a JBX 6300FS Electron Beam Lithography System (*JEOL, Ltd*) with an acceleration voltage of 100kV, beam current of 1nA and a base dose of 950µC/cm². The high atomic weight of the selected optoelectronic substrate material InGaAs / GaAs (as opposed to traditionally used silicon) amplified the electron scattering and thereby the spread of energy leading to a strong proximity effect. The required proximity effect correction (PEC) adjusts the exposure dose as a function of pattern density so that the desired column arrays can be transferred 1:1 from the layout to the specimen. The PEC was performed by the *Beamer* software (GenISys GmbH) using a Monte-Carlo simulated Point-Spread Function (PSF) [3] plus additional process blur typical for HSQ [2]. The experiments showed that the PEC adjusted exposure dose for small features (50nm and 30nm) was insufficient to adequately adhere the HSQ negative resist to the substrate during development, causing features to break away and wash off during resist development. In order to solve this issue, a cationic adhesion promoter, *SurPass 3000* (DisChem, Inc.) was introduced to the fabrication process. Devices were created by EBL on substrates with and without this adhesion promoter in order to test the feasibility of creating the nano-structures at lower doses while maintaining sufficient adhesion to survive the resist development process step.

3.1 Device Design

An array of columns consisting of four 100μm x 100μm quadrants was designed. Within each quadrant, the column dimension was 30nm, 50nm 100nm or 200nm respective, at a constant pitch of 400nm (see Figure 1). The quadrants are separated by a border of 5 microns of material. The border frames are required for automatic recognition of the subsequent optical measurement by NSOM. The layout data was prepared for e-beam exposure using the *Beamer* software (*GenISys GmbH)*.

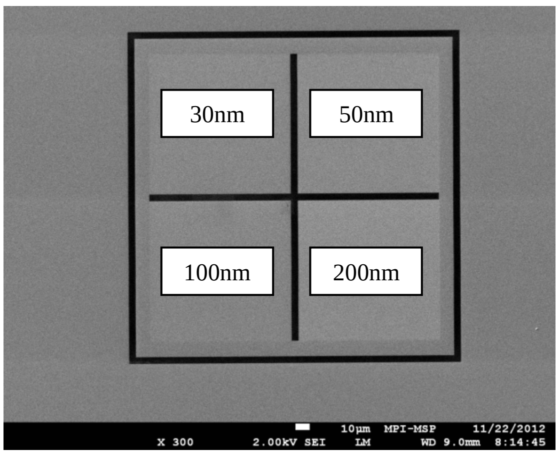

Figure 1
General View of Experimental Test Pattern
as Imaged by SEM (labelled for column diameter)

3.2 Manufacture of Device

The nano-columns within each quadrant on the device array were made using e-Beam exposure of HSQ negative resist on a multilayer InGaAs system. After development of the HSQ mask (SiO_2), the layout was transferred into the substrate by RIE (Reactive Ion Etching). The manufacturing flow of the device is summarized below:

- The desired pattern is created in HSQ resist by EBL

- Development of the exposed HSQ. The developed resist creates a mask surface of InGaAs valleys and SiO_2 mountains
- The pattern is subsequently transferred into the substrate (InGaAs on GaAs) by means of reactive ion etching (RIE)
- The remaining HSQ (SiO_2) was removed by diluted HF, leaving the desired columns built in the InGaAs / GaAs

The processed InGaAs multilayer system on GaAs is illustrated in Figure 2

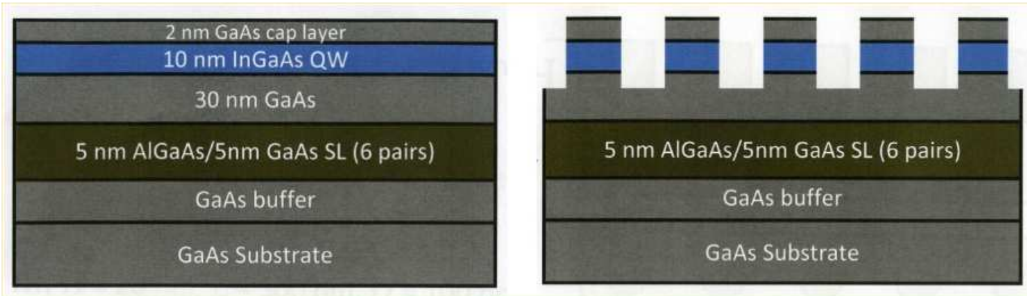

Figure 2
InGaAs multilayer system on GaAs before and after ELB an RIE processing

The *Beamer* software (*GenISys GmbH)* allows for highly accurate proximity effect correction, with PSF input that includes electron scattering (Monte-Carlo generated), and while the HSQ resist process effects [2] were reasonably good, extremely high dose values were required for the manufacturing of the nano columns. This could not be explained solely by proximity effect from electron scattering. The total exposure doses after PEC correction were 1.000 µC/cm² for 200nm column, 1.500µC/cm² for 100nm columns, 3.000µC/cm² for 50nm columns, and 8.000µC/cm² for the 30nm column arrays. While the arrays with the 200nm and 100nm pillars resulted in the dimensions as designed, the 30nm and 50nm pillars could not be resolved (all resist removed) at all. SEM pictures showed that the 30nm and 50nm columns had been formed, but that the adhesion to the substrate was not sufficient to hold the structures in place during the resist development process. In order to get these smaller columns to stick to the substrate they had to be over-dosed at very high levels (up to 30.000µC/cm²) resulting oversized resist features (>50nm instead of the designed 30nm) on the sample. Hence the creation of 30nm and 50nm columns in the desired design was not possible. Only through the introduction of a substrate priming agent, *SurPass 3000 Microlithography Adhesion Promoter* (DisChem, Inc.), could this be achieved. By improving adhesion of the HSQ resist to the substrate, *SurPass 3000* allowed the electron dose to be reduced sufficiently (8.000 µC/cm² for 30nm features). As a result it became possible to create the desired small column arrays with the required properties.

3.3 Design of Experiment

The effects of improved adhesion of HSQ negative resist on InGaAs / GaAs substrate were investigated by creating a test pattern using EBL. Specimens were processed with and without *SurPass 3000* treatment to evaluate the improvement in process latitude. *SurPass 3000* treatment is very simple: the cleaned specimen substrate was dipped for 60 seconds into the *SurPass 3000* solution, followed by a de-ionized water rinse and dried with nitrogen gun [4]. The substrate was then spin-coated with the HSQ e-beam resist. *SurPass 3000* is a water-borne, non-hazardous, cationic surface active agent believed to function through interaction with and modification of the substrate surface energy, optimizing the zeta potential [5] and allowing for greatly improved adhesion between the substrate and the resist without affecting the properties of the substrate itself. No deposition or physical changes to the substrates were evident when treated substrates were examined by x-ray photoelectron spectroscopy (XPS).

3.4 Findings and Results of Experiment

The test pattern (Figure 1) has been exposed on substrate without surface treatment at different dose levels after performing PEC with typical parameters, expecting that at the right dose (Base Dose) resolves all features as designed. However the exposure results showed that at doses that resulted in the 200nm columns (lower right quarter of layout) and the 100nm columns (lower left) on size, the 50nm columns (upper right) are only partly existing and the 30nm columns (upper left) are not existing at all as shown in Fig 3.

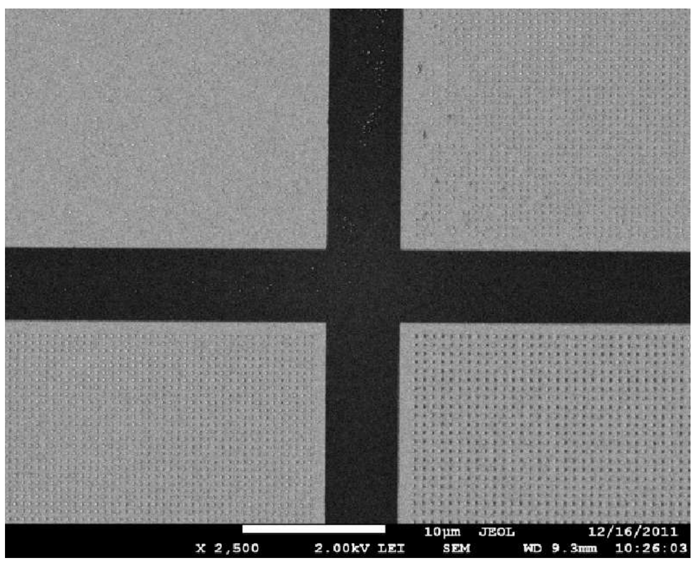

Figure 3
Overview of specimen array NOT treated with SurPass 3000
shows missing and misplaced columns in both the 30nm and 50nm quadrants.

This leads to the conclusion that the exposure dose for the 50nm and 30nm columns are too low. For printing the field of 30nm columns the dose had to be increased to the level of 30.000 µC/cm² leading to clearly overexposed (oversized to > 50nm) pattern in the center of the field and still missing columns in the corners (see Fig 4). This experiment also clearly showed that the "missing" columns had been formed and "washed away" during development. Figure 4 (b) is showing such cumulated columns spread over the sample surface. It has been observed that those columns had been oversized (to high dose) already.

This experiment clearly indicated that it is not possible to get 30nm columns by adjusting the dose, but the adhesion issue needs to be solved.

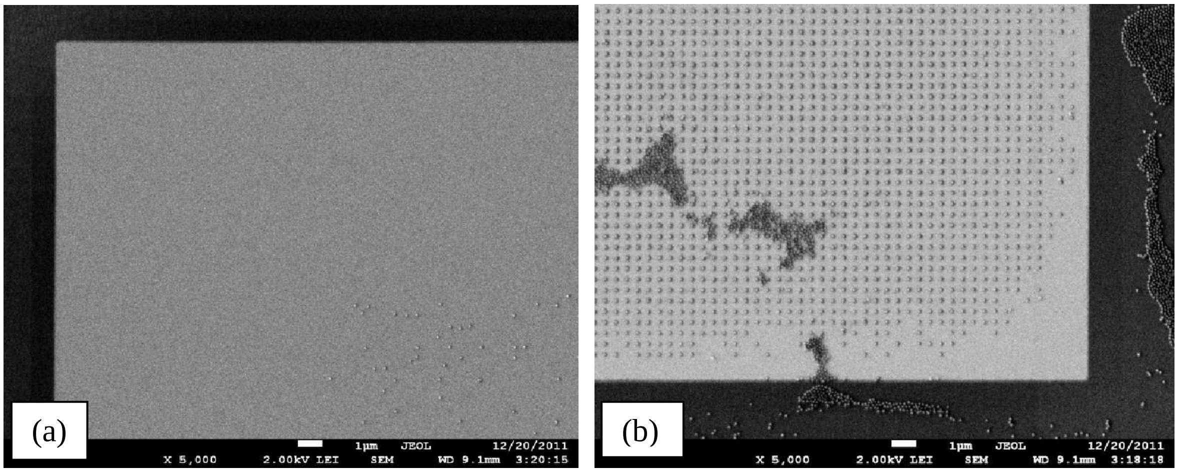

Figure 4

Upper left corner (a) and lower right corner (b) of the 30 nm field exposed with high dos on untreated substrate showing oversize in the center, missing columns in the corners of the field and columns which have been "washed away" and spread over the sample.

Substrates treated with *SurPass 3000* adhesion promoter showed a dramatic improvement in structure integrity, allowing for successful creation of structures at the 30 nm level. The issue of "washing away" small features is resolved so that they can be exposed at lower doses (30nm dots at 8.000 µC/cm² instead of 30.000 µC/cm²). The exposure using PEC is showing an excellent match of pattern sizes to design and high uniformity over the field (center to corner) for all sizes. Figure 5 shows the resist result after exposure and development with a good adhesion of all columns, including the 30nm columns (Figure 6).

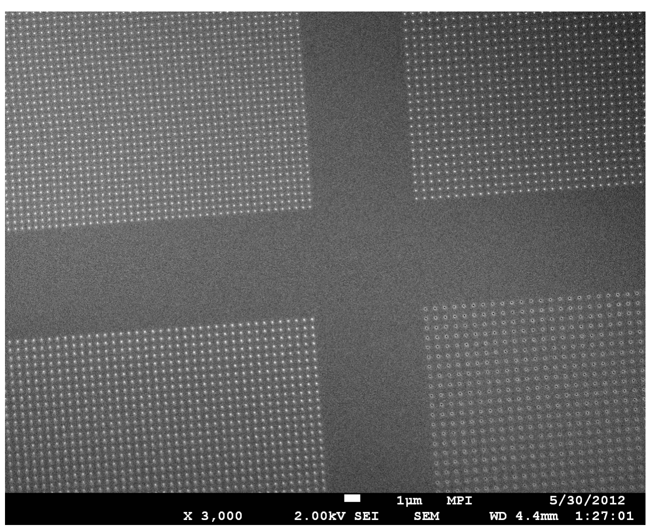

Figure 5

InGaAs wafer treated with SurPass 3000 prior to application of HSQ resist.
All structures successfully created.

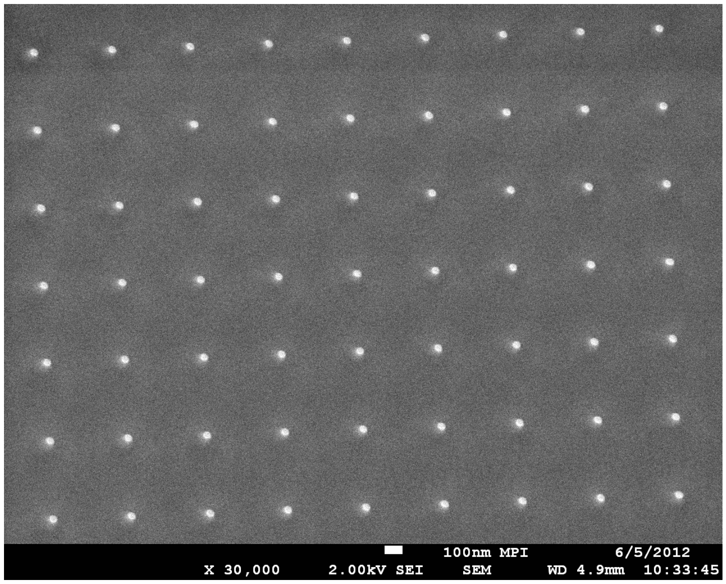

Figure 6
30nm lithographic structures on InGaAs wafers treated with SurPass 3000 prior to application of HSQ resist.

The resist pattern could be successfully transferred into the InGaAs / GaAs substrate resulting in a high quality test pattern for determining the accuracy of Near Field Scanning Optical Microscope.

4.0 CONCLUSIONS:

In an attempt to manufacture a device for measuring the accuracy a Near Field Scanning Optical Microscope (NSOM), it was found that the chosen optoelectronic material (InGaAs / GaAs) in combination with HSQ resist patterning was limited by adhesion issues.

Though the strong proximity effects for this high density material stack could be corrected (PEC) using the proven and accurate *Beamer* software (*GenISys GmbH)*, extremely high dose values were needed to get the small resist columns to adhere the substrate during development. The overdosing limited the resolution of the pattern to > 50nm and limited the uniformity over the field.

This adhesion issue could be solved by application of a cationic organic adhesion promoter, *SurPass 3000* (DisChem, Inc.) so that also the small features could be exposed without the need to overdose. With Surpass 3000 and using *Beamer* PEC the whole pattern could be manufactured with high accuracy of column sizes and a high uniformity needed for device.

X-ray photoelectron spectroscopy (XPS) analysis after application of Surpass 3000 has shown that there is no deposition, chemical, or physical changes of the material. The effect seems to be the change of surface energy, allowing for greatly improved adhesion between the substrate and the resist without affect the properties of the substrate itself.

Literature:

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