Nanogaps for fabrication of Molecular Devices

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ABSTRACT

Measuring the electrical properties of single atoms or molecules very often require either sophisticated techniques based on scanning probe microscope, or special contacting schemes which often limit experimental flexibility. In this article we report two different approaches to fabricate nangaps, namely, (a) two angle evaporation and (b) shot modulation. Utilizing these nanogaps fabricated on oxidized aluminium gate, we are capable of exploiting the quasi one-dimensional nature of these materials in combination with e.g. self assembling techniques, surface treatments and nanolithography for device functionality. Experimentally we have demonstrated to achieve sub 5 nm gaps both by two angle evaporation technique and shot modulation technique and compared their yield in nanogap fabrications.

Keywords: electron beam lithography (ebl), e-beam evaporation, nanogap, self-assembly, shot modulation.

1 INTRODUCTION

One of the most important technological difficulties that have been identified to fabricate various types of nanoscale devices based on non-conventional materials such as molecules and clusters is fabrication of nanogaps with predictable gap size. Obstacles also remains related to contacting schemes for attaching molecules or clustsers in the nanogap. The primary techniques that are utilized to characterize the electrical properties of single atoms or molecules are either based on scanning probe microscope, or special contacting schemes. Example of the later is demonstrated by Reed et. al. by measuring the electrical conductance of benzene.-dithiol molecules using mechanical break junctions to facilitate two metallic contacts [1]. The disadvantage of this approach is not to be able to introduce a gate electrode, which could broaden the experimental possibilities. Lately, Manako et. al. have demonstrated 7 nm wide line patterns by electron beam lithography (EBL) with a newly developed organic resist called Calixarene [2]. Chen et. al. had the approach to combine the lift off and wet chemistry to reach down to sub-10 nm structures [3]. Simpson et. al. succeeded to reach down to 6 nm gap between the electrodes by combining the EBL and reactive ion etching (RIE) techniques [4]. Gentili et. al. has fabricated 5 nm gaps by utilizing the mechanism of nanogap compression of PMMA resists during gold electroplating process [5]. Gribov et. al. made a novel approach to fabricate hole down to 10 nm by etching a nitride window [6]. Morpugo et. al. had demonstrated a chemical approach to reach nanogap of 1 nm with a good level of reproducibility [7]. McEuen et. al. have measured the transport properties of single nanoclusters by fabricating nanogaps using the method of shadow evaporation [8]. Nanogaps made by mechanically controlled break junction were demonstrated by Muller et.al. [9]. Hence, all this efforts have been made to meet the future technological challenges in miniaturizing the electronic devices.

We have explored the shot modulation technique to define the nanogap dimensions using electron beam lithography which was found to be more advantageous over the two angle evaporation technique. The shot modulation technique has been proven to be a robust technique to be used for fabricating different kinds of nanostructures. For example, by varying the dose applied during the exposure of two closely spaced electrodes, the width of the gap between them can be controlled with nanometer precision [10]. Utilizing these nanogaps fabricated on oxidized aluminium gate, we are capable of positioning the nanoelements through functionalization schemes like self assembling techniques, surface treatments and nanolithography for device functionality. Thus the quasi one-dimensional nature of these materials can further be explored.

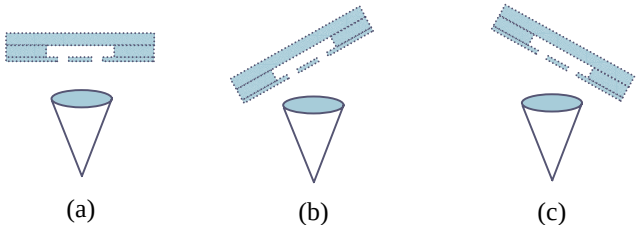
2 EXPERIMENTS

We had two different approaches to fabricate nanogaps though there are different ways of accomplishing this target, namely, (a) two angle evaporation and (b) shot modulation. We have used the high resolution Electron Beam Lithography (EBL) system, Model JEOL JBX-5DII, which has the minimum spot size of less than 10 nm at its best condition.

2.1 Two angle evaporation technique

The first method to fabricate nanogaps pursued was the two angle evaporation demonstrated by McEuen et. al. We used a double layer of co-polymer and poly (methylmethacyrlate) (PMMA) resist system in the fabrication process. 6% Copolymer in Ethyl Lactate was spun at the rate of 4000 rpm to form a 140 nm thick resist and subsequently baked at 170^0C for 5 minutes on a hotplate to promote good undercut and suspended bridge of PMMA. After the wafer is cooled, molecular weight of 950k 2% PMMA in Anisole was then spun on the wafer at

4000 rpm for 1 minute and subsequently baked at 170^0C for 5 minutes on a hotplate. High baking temperature is suggested to improve the adhesion to the substrate [3].



(a) (b) (c)

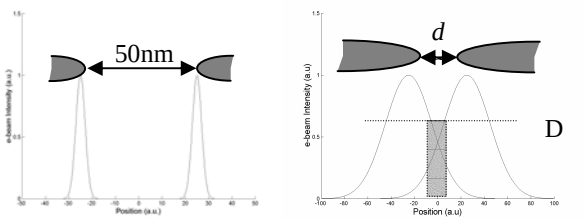
Figure 1: Three different angles for evaporation.

Development time was then optimized to get a suspended bridge of PMMA which act as a shadow mask for angle evaporation. ECA and Ethanol (1:5 ratio) and Toluene and IPA (1:3 ratio) was used as the developer for the PMMA and the Co-polymer respectively. The sample was immersed into the PMMA developer for an optimized value of 10 seconds and subsequently immersed into IPA solution for ~5 seconds and finally dried with N_2 blow. Afterwards, the sample was immersed into the Co-polymer developer for 25 seconds with subsequent immersion in the IPA solution for ~5 seconds and finally dried with N_2 blow. It was found that immersion into the co-polymer developer for 25 seconds was enough to form the suspended bridge of PMMA.

After e-beam exposure and development a layer of 10 nm Cr/NiCr and 50 nm of Au is evaporated sequentially in an e-beam evaporator. Prior to the mounting of the sample in the metal evaporation chamber, wafers were exposed to 50 watt O_2 plasma for 15 to 30 seconds at 250 mTorr pressure and 160 DC bias. After metallization, lift off was carried out in Acetone at 50^0 C, IPA, DI water and blown dry with N_2 consecutively.

2.2 Shot modulation technique

The second method used for fabricating nanogaps was shot modulation. This method was based on (a) the variation of e-beam dose and (b) optimization of the development time of the polymer. By this method we have achieved sub 5nm gaps rather reproducibly. 10% Copolymer in Ethyl Lactate was spun at the rate of 6000 rpm to form a ~320 nm thick resist and subsequently baked at 150^0C for 5 minutes on a hotplate to promote good undercut. After the wafer is cooled, molecular weight of 950k 2% PMMA in Anisole was then spun on the wafer at 6000 rpm for 1 minute (45nm thick layer) and subsequently baked at 150^0C for 5 minutes on a hotplate. After e-beam exposure, the pattern was developed in conventional IPA/H_2O (93:7) developer system. After O_2 plasma treatment, metallization was carried out by e-beam evaporation of 5 nm Cr and 10 nm of Au at a certain angle with respect to the metal source.



(a) (b)

Figure 2: Shot modulation profile: (a) at nominal dose where the Gaussian beam intensity for two electrodes pattern is well defined, (b) at critical dose where Gaussian beam intensity becomes significant in determining the actual electrodes gap.

Following this process, narrow gaps were fabricated by gradually incrementing the e-beam dose by 5% or 10% starting from low dose of 150 μC/cm^2 to upward until we see the smooth transition from 50nm gap to shorted nanolids. In the figure 4 we observe the smooth transition of nanogaps from 50 nm to shorted electrodes. This provides a way to fabricate any gap between 50 nm and 0 nm depending on the facts like (a) minimum size of PMMA molecules and (b) source of metallization. It is very important to have a point like source for metallization to avoid short circuit instead of nanogaps due to the solid angle of the metal source.

3 RESULTS AND DISCUSSIONS

In order to accommodate preferably a single molecule the requirement is to achieve nanogaps of less than 5 nm. However, a number of parameters that ultimately sets the resolution of the fabricated nanogaps which includes (a) resists, (b) e-beam acceleration voltage (c) substrate and proximity effect, (d) incident angle of metal evaporation, (e) substrate temperature during metal evaporation and (f) diffusion of the evaporated metal(s) etc.

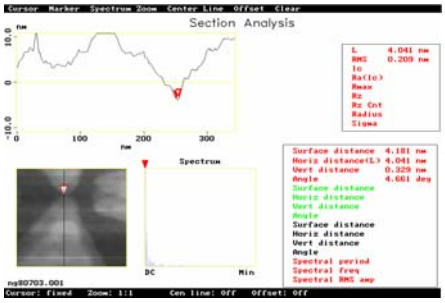


Figure 3: AFM characterization of nanogaps formed by two angle evaporation. a gap of < 5nm is measured from the cross section analysis.

Figure 3 is the atomic force microscope (AFM) topography of one of the nanogaps fabricated by two angle evaporation

technique. The source, drain and the lateral gate electrodes are visible at the bottom left picture. The cross section analysis of the fabricated gap showed < 5 nm gap between the electrodes.

The experimental results obtained from the shot modulation technique are shown in a series of picture in figure 4. The observation in this case in figure 4 can be explained with the help of the figure 2. In figure 4 (a) 50 nm gap is shown for a specific dose. With a certain increment (10% in this case) of the dose, the e-beam overexposes the resist at the tip of each electrode and thus resist in the inter-electrode region is also partially exposed. The Gaussian intensity profile of the e-beam with respect to dose increment is shown in the figure 2 (b) which explains how the predefined gap of 50 nm is shrinking down to the 0 nm or short circuit. When the Gaussian intensity profile of e-beam becomes equal or smaller than the actual beam size, both beams overlap in the gap region and the actual gap will then be defined by (a) the e-beam dose larger than a threshold value D_t, (b) development time t_{dev} in the subsequent development process and (c) minimum molecular length of the resist.

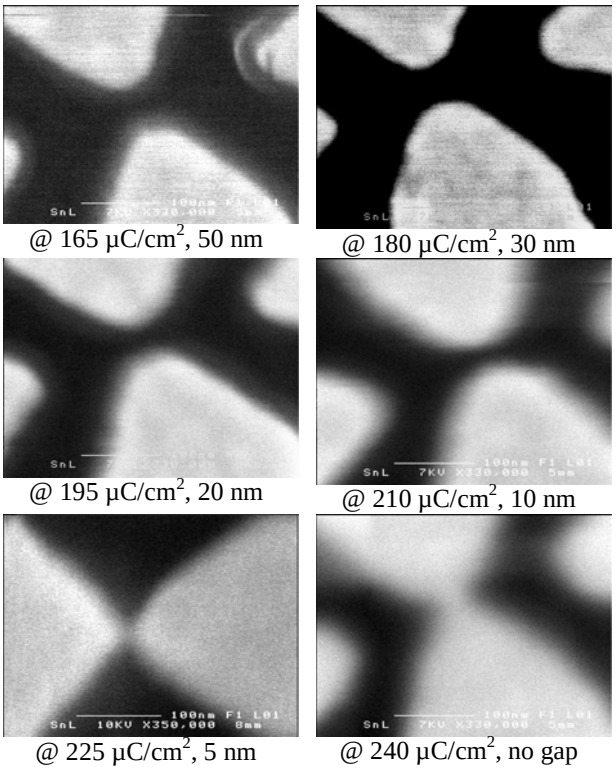


Figure 4: Reduction of inter distance between the electrodes from 50 nm to no gap.

In the following table the characteristics of different methods used for producing nanogaps are recapitulated. As it appears, the shot modulation technique is superior and simple method to produce reproducible results compared with the two angle evaporation technique. Uncertainty exists for both the methods but the yield of shot modulation technique is much higher to obtain gaps below 5 nm in an experimental run.

Items for characterization	Angle	Shot modulation
Resists system	2%PMMA 6% Co-polymer	2% PMMA 10% Co-polymer
Metallization	Cr/Au, NiCr/Au	Cr/Au
Best achievement	~4 nm electrodes spacing	~2 nm electrodes spacing
Yield	Poor	Better (>80%)
Limiting factors	Sample rotator, Metallization source	Chain length of the resists, Metallization source

Table 1: Characteristics of nanogaps manufactured by different methods are compiled for comparison.

Figure 5 shows the surface morphology of a device after clusters assembling. The clusters were capped with thiol terminated carbon legands to facilitate self assembly with gold electrodes. We observe a trend of clusters conglomeration in the vicinity of the nanogaps. More interestingly, two of such conglomerated structure showed field effect behavior [11]. Conglomeration of gold clusters was also observed outside the nanogaps. The surface roughness of the source/drain (gold metal in our case) is increased compare to the fresh electrodes. From the cross section analysis, the surface roughness was found to be < 3 nm for the freshly made source/drain. On the other hand, after the chemical treatment, the surface roughness increased to 10-15 nm which means that the clusters are aligning on the gold surface.

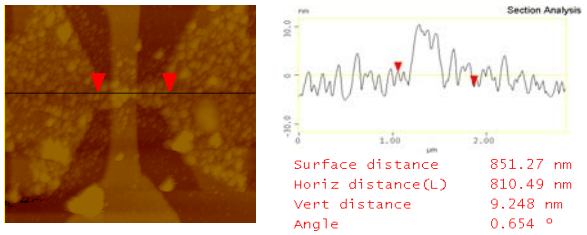


Figure 5: Cross section analysis of the AFM image shows the surface roughness to be 10-20 nm after self assembly of gold clusters capped with thiol terminated legands.

In self assembled monolayer (SAM) based electronics, the structure and binding of thiol molecular linkers to gold surfaces and nanoparticles is the core to the understanding of the electronic properties of the system [12, 13] The study

of mono-molecular electron transport generally requires consideration of bonding with irregular metallic contacts or poorly defined surfaces such as break junctions, electromigration generated gaps, and scanning probe microscopy tips. These structures can locally bear a closer resemblance to atomic clusters, as compared to neat metallic surfaces. Thus the prediction and understanding of the electronic transport properties for molecular wires and nanoscale assemblies requires detailed knowledge of thiolate-gold cluster interactions. However, theoretical calculation revealed that the sulfur atom largely determines the bonding to gold and it appears that the type of organic molecule that is attached to the sulfur is of minor importance to the bonding [12]. The energy levels in the bonded complex corresponding to the molecular HOMO and LUMO undergo shifts in energy. Recent investigation performed on such devices made by the followed methods revealed nanoelectromechanical behavior originated from agglomerated clusters with organic legands [11].

4 CONCLUSIONS

We have fabricated and evaluated two different methods to fabricate nanogaps for molecular devices based on molecules and clusters. Despite the uncertainity exists for both methods for nanogap fabrication, the shot modulation technique found to be superior to the two angle evaporation technique. Thus the nanogap fabrication technique by shot modulation technique opens up the possibility to explore the quasi one-dimensional nature of nano materials for electronic devices.

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