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Nanometer scale high-aspect-ratio trench etching at controllable angles using ballistic reactive ion etching

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We demonstrate a low pressure reactive ion etching process capable of patterning nanometer scale angled sidewalls and three dimensional structures in photoresist. At low pressure the plasma has a large dark space region where the etchant ions have very large highly-directional mean free paths. Mounting the sample entirely within this dark space allows for etching at angles relative to the cathode with minimal undercutting, resulting in high-aspect ratio nanometer scale angled features. By reversing the initial angle and performing a second etch we create three-dimensional mask profiles.

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I. INTRODUCTION

As the dimensions of semiconductor devices decrease, it becomes increasingly more important to precisely control dopants at the nanoscale level. Retrograde doping in MOSFET devices to reduce short channel effects[1,2] and graded base doping in bipolar junction transistors for a reduction in base transit times[3] are just two examples of the importance of nanoscale impurity doping.

One method to achieve such precision with homogenous implants is to use high-aspect-ratio structures in resist to serve as implantation masks. The high aspect ratio of these masks reduces lateral ion straggle and helps keep the implanted profiles sharp and well defined. For gradient doping, thermal diffusion is typically used to grade the profile which in practice is very difficult to precisely control at the nanoscale. In this work, we demonstrate a novel masking approach to achieve nanoscale gradient doping by fabricating a three dimensional mask using a multilayer approach based on electron beam lithography and ballistic reactive ion etching at angles. Furthermore, our process can be utilized for many other nanofabrication processes like MEMs devices and nanopatterning of complex oxides.

Reactive ion etching (RIE) is an established and widely used dry etching technique to selectively remove material from a surface. It is typically used in conjunction with a lithographically patterned resist spun on the sample surface in order to transfer a specific pattern into the substrate. A large parameter space consisting of process gas selection, pressure, temperature, and plasma power offer the adaptability to a vast range of applications in science and industry. The incident ions accelerated in the generated plasma are typically directed perpendicular to the sample surface which makes any attempt to perform RIE at an angle to the surface difficult. A few papers have been published on this specific issue[4–8] typically using complicated sample holders or faraday cages with the goal of creating a plasma dark space where the ballistic transport of ions ensures a high directionality. A tilted surface located inside this dark space will continue to be etched perpendicular to the cathode (typically the RIE sample holder) resulting in inclined sidewalls. While previous works were concerned with performing angled etches into substrate materials, here we demonstrate the creation of high-aspect ratio nanometric trench etching in resist at arbitrary (controllable) angles to the substrate. Our approach utilizes etching at pressures (< 4 mtorr)which is lower than most conventional RIE processes because at low pressure the mean free path of the ions

near the cathode becomes large (∼2 cm) naturally creating a dark space where directional high precision ballistic etching can be performed. This technique can also be used to create three-dimensional photoresist masks that can be employed to achieve complex doping profiles in materials when used as masks for ion implantation.[9,10] In addition, these structures may also be used as templates for the fabrication of nanoimprint masters.[11,12]

II. EXPERIMENTAL

The entire process is illustrated in Fig. 1. A trilayer [Fig. 1(a)] is built on the substrate material consisting of a thick hard-baked layer of photoresist (1.6 μm), an evaporated Germanium (Ge) layer (28 nm), and 100 nm of electron beam lithography (EBL) resist polymethylmethacrylate (PMMA). For this work we used silicon as substrates, however, it should be noted that the presented process can be performed on any substrate material that is compatible with the photoresist employed. For instance, this trilayer process has been successfully used on thin film superconductors such as $YBa_2Cu_3O_{7-\delta}$ on sapphire[13] and MgB_2 on silicon carbide.[14] In a subsequent step the topmost PMMA layer is patterned by EBL. A periodic array of long (up to several mm), parallel fine lines is transferred into the PMMA resist. For our samples we used a line spacing of 1 μm but in principle any line spacing within the lithography capability is possible. The patterned trilayer is then subjected to dry etching in chlorine based plasma to perform breakthrough of the germanium layer. While PMMA is also etched in the chlorine plasma the small thickness of the germanium layer allows for a short time etching process which ensures that about two thirds of the initial PMMA film is still present after this RIE step, effectively protecting any underlying germanium. In addition to providing excellent etch selectivity to photoresist evaporated germanium is very amorphous with no granularity on the nanometer scale. This ensures well defined nano features. For the trench etching into the photoresist, the substrate is tilted at a chosen angle to the RIE sample plate and etched in low-pressure oxygen plasma [Fig. 1(b)]. The germanium layer is not etched chemically in oxygen and thus serves as a mask for the underlying photoresist. It is important to note that the substrate must be located entirely within the dark space of the oxygen plasma. Only in this region are the ions ballistic, hence the ions in the plasma are highly directional and able to produce high aspect-ratio trenches.

Several different right angle sample holders were fabricated by machining small aluminum

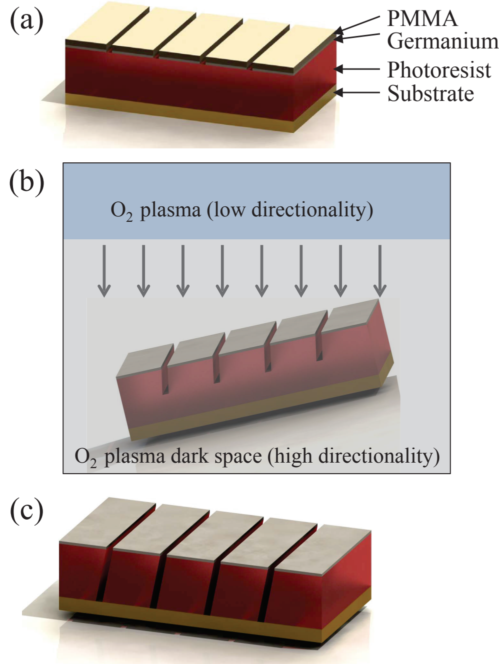

FIG. 1. (Color Online) RIE process to create nanoscale high aspect ratio trenches. (a) A trilayer is built on the substrate material consisting of 1.6 μm photoresist, 28 nm germanium, and 100 nm of PMMA. (b) Using EBL and chlorine dry etching, a periodic line pattern is transferred into the Ge layer and the sample is subsequently etched using low-pressure oxygen plasma within the dark space at an arbitrary angle to the RIE sample plate. The remaining germanium layer is not chemically attacked by oxygen and preserves the EBL pattern to serve as a mask for the underlying resist. We note that the topmost PMMA layer is also removed in this step. (c) A periodic array of inclined trenches is created.

triangular sample mounts consisting of a single inclined surface. The heights of the wedges were kept small to ensure that they were entirely in the dark space of the plasma. They ranged between 4.7 to 8 mm for the various angles. The samples were attached using a 1:1 mixture of Apiezon N grease and Dow Corning 340 heatsink compound to the sloped surface of the triangles and were subsequently placed on the RIE sample plate. The germanium was etched at room temperature in 25 mTorr of CCl_2F_2 gas at 50 W for 100 s. No external bias was applied and the plasma DC self bias was 50 V. Subsequently oxygen etches were performed at room temperature at a pressure of 4 mTorr at 100 W for 900 s. No external bias was applied and the plasma DC self bias was 300 V. The low plasma pressure ensured minimal undercutting and resulted in sub-30 nm wide etched canyons featuring a very high

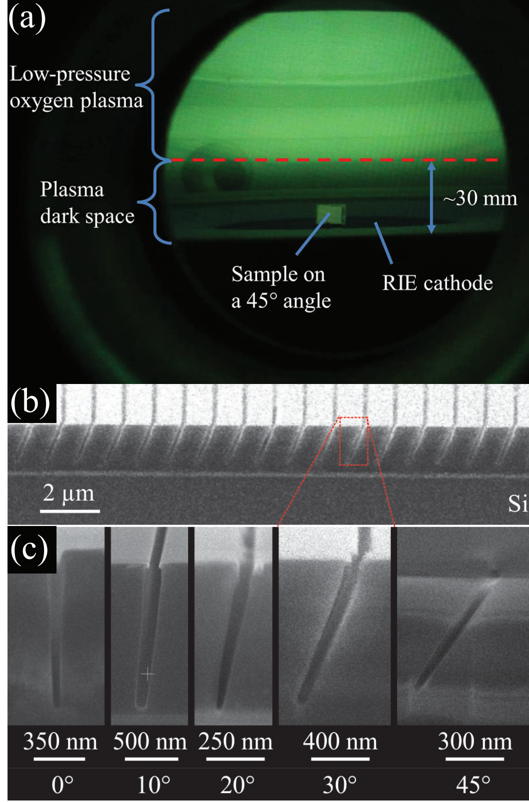

FIG. 2. (Color online) (a) Optical photograph showing a sample etched in the darkspace on a 45° angle. (b) Cross-sectional SEM images of the cleaved surfaces after etching. Line array with a line spacing of 1 μm after etching at 30° angle. (c) Magnified images of individual trenches etched at different RIE angles (indicated at the bottom).

aspect-ratio. Fig. 2(a) shows an optical image of a sample being etched on a 45° angle. For inspection of the etch profiles the silicon wafer pieces have been cleaved perpendicular to the etched line array and mounted on a 90° scanning electron microscope (SEM) sample holder. This ensured that the cleaved surface faces the SEM pole piece and hence cross-sectional images of the etched trenches could be recorded. Fig. 2(b) shows a typical cross-sectional image at near 90° viewing angle of a cleaved surface with an etched line array. The angle during etching used in this case was 30°. The etched trenches display high uniformity. Magnified images of individual etched trenches illustrated in Fig. 2(c) reveal that the angle during etching (displayed at the bottom in Fig.2(c)) is not reflected exactly in the actual trench angle. This is in agreement with Coldren et al[5] who also reported an offset between the angle during etching and the resulting angle. However, in contrast we did not notice any difference in etch rate between any of the investigated angles. Fig. 3 illustrates the

measured trench angle as a function of the etching angle. Rather than a fixed angle offset a linear dependence can be observed showing a slope of 0.81. This would predict a theoretical maximum trench angle of 73°. It is to be determined if this relation is generally valid or simply a property of the RIE tool or process parameters used.

A triangular three-dimensional mask profile can be created by reversing the initial angle and repeating the oxygen plasma resist etch. The process is illustrated in Fig. 4. The sample is initially etched at the first angle [Fig. 4(a)], followed by a second etch process at an angle performed in the opposite direction [Fig.4(b)]. Additional lines perpendicular to the line array are one way to ensure successful lift-off [Fig.4(c)] of the upper level of photoresist after the second etch. Sem pictures of a symmetric mask created by etching at 60° followed by 150° is shown in [Figure 5(a,b)]. For this sample we chose a 1 μm periodicity of our line array which resulted in a 350 nm tall structure. Using other combinations of etch angles produces different mask profiles (e.g. a sawtooth profile when using 0° angle during the second etch process).

One application of the presented three-dimensional mask profiles is to create nanometric graded doping profiles in the substrate by subjecting it to uniform high-energy ion implantation. These profiles can be symmetric by using the same angle for both etches or asymmetric by utilizing different angles for each etch. During ion implantation, thicker mask regions will block incident ions from reaching the substrate resulting in low or no doping (when the mask is thick enough to fully absorb the impinging ions). Thinner mask regions will result in a high substrate doping. The final doping profile can further be adjusted by using different

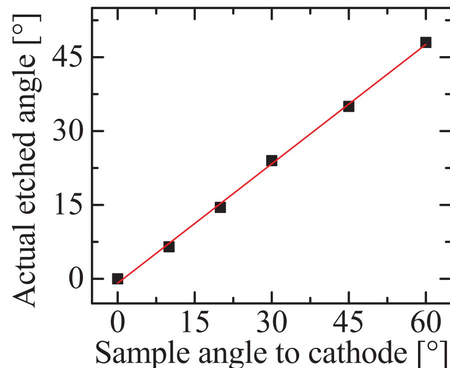

FIG. 3. (Color online) Measured trench angle as a function of angle during etching. The resulting linear dependence displays a slope of 0.81.

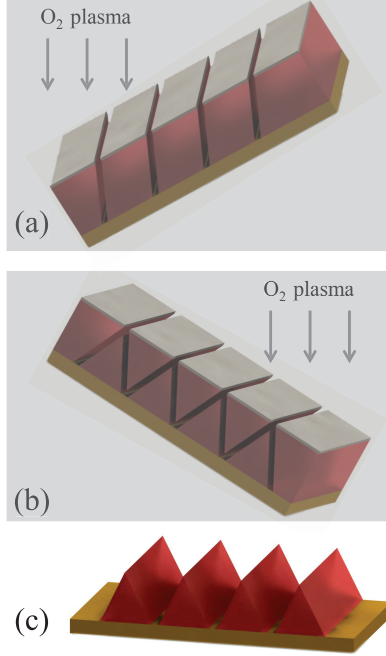

FIG. 4. (Color online) Creation of three dimensional structures in resist using a double angle etch process. (a) The sample is first etched at an angle. (b) The angle is reversed and the oxygen photoresist etch is repeated. (c) After lift-off a three dimensional structure remains.

implant angles, doses, energies, and ion species. Furthermore, anneals may be performed after stripping the mask which is easily done with acetone.

III. CONCLUDING REMARKS

In conclusion, a dry etch process using reactive ion etching has been presented that is capable of creating angled high-aspect-ratio trenches and sidewalls. This is achieved by using a low-pressure oxygen etch approach to pattern a trilayer mask that is placed entirely in the plasma dark space during processing. We have shown that arbitrary angles can be used although the actual etched angle is about 20% smaller than the angle between the RIE cathode and sample during etching. In addition, by reversing the angle in a second etch step it is possible to produce three-dimensional mask profiles which can be used as masks for ion implantation, MEMS devices, and patterning of materials that may only be sputter etched such as complex oxides like high transition temperature superconductors, or manganites.

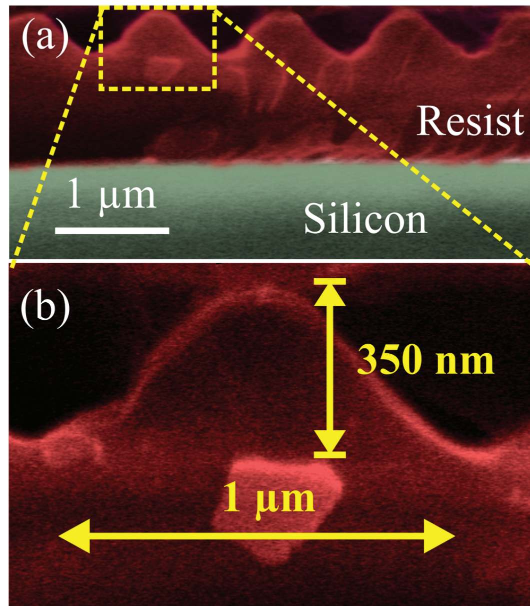

FIG. 5. (Color online) SEM images of a three dimensional mask created by a double angle etch process. (a) Five periods of a line array etched at 60° followed by 150° after lift-off. (b) Zoomed view showing the dimensions of one structure.

ACKNOWLEDGMENTS

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