Applications of new focused ion beams in nanofabrication and material studies

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INTRODUCTION
The abilities and applications of focused ion beam (FIB) methods appear to be limitless. System users are discovering more ways to create unique three-dimensional structures from ion-beam processing. Throughout the literature [1-3 and references within], FIB has traditionally employed elemental gallium as an ion source due to its liquid metal state just above room temperature, low volatility, low reactivity with the needle material, low vapor pressure, and excellent vacuum and electrical stabilities. This seems to meet the needs for the majority of FIB users and applications. While there are several focused ion-beam tools meeting many of conventional users needs (TEM sample preparation, slice and view 3D characterization, single process step applications), many of these are not feasible for step and repeat processing over large areas and do not offer other options for ion sources. The use of non-gallium ion beams has also endured for over 20 years [4-7], but the number of these tools is small compared to the gallium ion source tools operating today and most are home built by the laboratories operating them.

In this article, we report on the results of engaging non-gallium ion species for shaping traditional compound semiconductors of Ga-group V.

ION BEAM LITHOGRAPHY

SYSTEM OVERVIEW
The system used here is a lithography-based FIB tool capable of direct-write patterning with a nanometer-scale beam spot, sample position accuracy over large areas, and long duration stability. To enable this functionality, three factors of the system must maintain extremely high stability and accuracy: the ion source, the ion column, and the sample stage.

The stage is a laser interferometer system designed for nanometer-scale reproducibility and low drift enabling this system to excel at lithography over more conventional FIB systems. The ion column is capable of beam energies of 15-40 kV and provides a beam current stability of less than 1% change per hour. This particular column design allows for an additional aperture and mass filter (Wien filter) to be inserted between the beam limiting aperture and stigmator which permits liquid metal alloy ion sources (LMAIS) to be employed.

The mass filter is a mass trajectory filter separating the paths of different ion masses based upon the applied electric field, the permanent magnetic field and the velocity of the ions. The beam crossover position within the Wien filter affects the beam spot and the mass resolution. Best imaging resolution mode, which supplies the smallest spot size, occurs when the beam cross-over is located within the center of the Wien filter. Best mass resolution mode, which supplies the largest mass separation, occurs when the beam is at cross-over at the lower aperture [8]. The position of the beam cross-over in the Wien filter is controlled by the condenser lens setting.

The LMAIS selected for this reported work is an AuBeSi eutectic. This source provides a wide range of ions for milling, doping, surface modification, chemical vapor-assisted deposition and imaging. For example, Si is a common n-type dopant and Be is a p-type dopant in III-V semiconductors. An example mass spectrum from our AuBeSi LMAIS is shown in Figure 1. As one can see, there is a wide host of ion options emitting from the single alloy source with Au being the majority of the ions emitted. Doubly charged ions and ion clusters further expand the capabilities of the system by allowing effectively higher and lower ion energies, respectively. All of this widens the possibilities of materials processing over a traditional Ga source FIB.

MATERIALS PROCESSING
Gallium arsenide (GaAs) is the most widely used compound semiconductor material and its application has benefitted from FIB processing and modification [9-11]. Several other semiconductors in the Ga-group V family have also benefitted from FIB technology as well. The processing of Ga-group V material with Ga’ ion beams results in a high density of Ga droplets forming on the milled surface and in some instances, a very roughened surface morphology. Techniques to remove these Ga droplets include in-situ gas-assisted etching with iodine [12], cryostage use or post-FIB etching. We investigated processing III-V semiconductors with an Au ion beam and a Si’ ion beam to determine if a cleaner milling surface was feasible without requiring extra processing. For
the purpose for this report, we limit our materials list to GaAs, GaP and GaN.

FOCUSED ION BEAM LITHOGRAPHY

Samples were clip-mounted to the stage holder and loaded into a Raith ionLINE multiple-species focused ion-beam instrument. The chamber base pressure was 10^{-7} Torr and column pressure was below 10^{-8} Torr. The working distance for all the reported data was 10 mm and the ion column was normal to the sample surface.

SCANNING ELECTRON MICROSCOPY

Scanning electron micrographs were obtained using an FEI Nova SEM with field emission and thru lens secondary electron detection. Samples were removed from the ion beam system and were imaged without any post milling processing or coatings.

RESULTS

MATERIALS SHAPING

A sample of undoped, semi-insulating (001) GaAs was milled with a 30 kV Ga+ ion beam in an ionLINE system without a Wien filter as a comparison to Au ion beam milling. Milling parameters such as beam current, dwell time and scan loops were altered to produce the lowest number of Ga droplets and smoothest sidewall and bottom features.

For the Ga+ ion-beam milling, the beam current was changed from 100 pA to 30 pA to 6 pA and the scan loops were varied from 100 to 50,000, while fluence was kept in the range of 30,000 µC cm^{-2} to 70,000 µC cm^{-2}. The lowest Ga droplet formation was found with a low beam current and lower scan loop counts. For scan loop counts over 20,000, the dwell time was too short for the pattern generator and beam blanker to manage, causing feature distortion. The effect of fluence seems to only affect the depth of the milled feature. Figure 2a is the result of a typical Ga+ ion milled feature in GaAs, this is similar to images found in the literature for Ga+ ion milling of GaAs. The fluence was 50,000 µC cm^{-2}. The depth of a 1 µm x 1 µm hole feature milled with these conditions is approximately 750 nm.

For the Au+ ion beam, the beam current was maintained at 30 pA and the scan loops were maintained at 100, while the fluence was varied in the range of 30,000 to 70,000 µC cm^{-2}. An example of this milling is shown in Figure 2b using a fluence of 50,000 µC cm^{-2}. There was no evidence of Ga droplet formation from the Au+ milling for this fluence or any fluence attempted. The effect of fluence is similar to the Ga+ ion milling, seems to only affect the depth of the feature milled. The depth of a 1 µm x 1 µm hole feature milled with these conditions is approximately 1400 nm, surprisingly almost two times deeper than the Ga+ ion beam milling under identical system conditions.

According to TRIM model calculations (www.srim.org/), the sputter yield of GaAs for a 30 kV ion beam at an angle of 0° (in terms of Ga:As atom yield, modeled at 1000 incident ions) is 2.92:6.35 for Ga+ ions and 3.42:7.61 for Au+ ions, showing that the use of heavier mass and shorter projected range results in higher material removal. Since the sputter yield for As is much higher than for Ga under both applied ions, we will focus on the sputter yield of the Ga atom from the GaAs and assume the As is not the limiting factor in the material sputter process for GaAs. We do however keep the target material as GaAs in the simulation model. Comparing the ratio of Ga yield for the Ga:Au ion ratio, we get 2.92:3.42. Or, for every one Ga atom removed by Ga+ ions we should expect to remove 1.17 Ga atoms with the Au+ ions, a 17% increase in milling rate. Our experimental results indicate that we are removing approximately 1.86 Ga atoms with the Au+ ions, a measured 86% higher milling rate for Au+ over Ga+.
shows a higher magnification view of a Au⁺ milled GaAs surface (pillar array), indicating the lack of droplet formation with this higher milling rate.

Performing these same experiments on substrates of (001) gallium phosphide (GaP) yielded similar results. The surfaces were Ga droplet free without any post-milling processing, cryostage use or in-situ gas assistance. A 1 µm x 1 µm hole in GaP milled to a depth of approximately 1000 nm with an ion fluence of 50,000 µC cm⁻² and beam energy of 30 kV. Performing TRIM simulations, the sputter yields of GaP for Au⁺ ions is 3.27:4.15 and 2.36:3.04 for Ga⁺ ions, both at 30 kV. Assuming again the Ga atom is dominate in the material sputter rate, we should expect to have a 38% increase in milling rate for Au⁺ over Ga⁺. The ion depth penetration for Au⁺ in GaP is 15 nm and 20 nm for Ga⁺ (both at 30 kV). Images of Ga droplet-free milled surfaces are shown in Figure 4.

These experiments were then performed on substrates of (0001) gallium nitride (GaN). We have seen a very low concentration to Ga droplets formed in milled structures when using a Ga⁺ ion source, however, we have not found any that are completely free of Ga droplets. When using the Au⁺ ion source, all of the milled structures were Ga droplet free. A 1 µm x 1 µm hole in GaN milled to a depth of approximately 900 nm with an ion fluence of 50,000 µC cm⁻² and beam energy of 30 kV. Performing similar TRIM simulations, the sputter yields of GaN for Au⁺ ions is 5.20:5.43 and 4.23:4.52 for Ga⁺ ions, both at 30 kV. Assuming again the Ga atom is dominate in the material sputter rate (especially since the group-V atom is N), we should expect to have a 23% increase in milling rate for Au⁺ over Ga⁺. The ion depth penetration for Au⁺ in GaN is 11 nm and 14 nm for Ga⁺ (both at 30 kV). It is interesting to note that while the simulated sputtered ion yield is higher for Au⁺ in GaN than for GaP, the measured milling rate in GaN is lower when comparing our 1 µm square hole comparison. This may be accounted for by the large difference in material density, 6.1 g cm⁻³ for GaN compared to 4.2 g cm⁻³ for GaP. One would expect the higher density material to melt at a lower rate. Images of Ga droplet-free milled surfaces of GaN are shown in Figure 5.

The lack of Ga droplets while milling with an Au⁺ ion beam seem to indicate that the droplet formation is more dependent on the ion species impinging on the surface and less on the previously published conclusion regarding group V element desorption from local heating or dissociation from milling [13]. This lack of droplet formation may be related to the implantation of Au in the subsurface at a much lower range compared to Ga implantation. This would cause a shallower damaged region and a smaller volume of amorphous material produced under the milled surface. In an amorphous material, the group V element would have a higher chance for sublimation and thus leave a Ga rich surface prime for droplet formation. An additional factor may also be that an Au⁺ ion has a higher sputter yield for pure gallium metal (8.02) than a Ga⁺ ion has for pure gallium metal (6.77), leading to more efficient removal of surface gallium in droplet form.

**MATERIALS SYNTHESIS**

Graphene formation on SiC via Si sublimation is a well-defined process [14, 15]. This sublimation process has a high thermal budget (1250-1350°C). This process is typically performed on large substrate areas to create uniform regions of graphene. During this process, SiC bonds are broken and Si atoms sublimate from the surface, leaving a carbon-rich surface that reconstructs to form a graphene layer. Ions of Au and Si were implanted into silicon carbide (SiC) employing the multiple-species focused ion-beam instrument [16,17]. By controlling the ion dose and energy, regions with shallow amorphous depths were created. These samples were then annealed in vacuum (10⁻⁶ Torr or better) up to 1400°C to form graphitic regions and graphene. Regions of implantation formed graphitic material at a temperature of 100°C to 150°C lower than non-implanted regions. This lower thermal budget was achieved due to the amorphous layer jumpstarting the SiC bond breaking process and possibly the implanted ion acting as a catalyst. Structural and Raman analysis indicate the unimplanted regions remain pristine SiC and the graphene regions were multilayer [16,17]. Figure 6 is an example of Au⁺-implanted regions in SiC (a) and the corresponding 2D Raman area.
map (b) post anneal. Limitations in the Raman mapping resolution required large areas for characterization purposes.

Attempts with a Ga+ ion beam to replicate the process have, to date, not provided the same results. This provides some evidence that the implant species may be providing some catalytic effect in addition to amorphizing the surface. By employing a nanoscale beam spot size, graphene nanoribbons and active regions have been “written” onto the surface to provide a maskless option for graphene device formation. This allows the remaining surface of the SiC wafer to be used for traditional solid state devices for future graphene integration into electronic devices. Further investigations are ongoing to refine this implantation enhanced process to create single layer graphene.

CONCLUSIONS
It has been demonstrated that there are advantages to using non-gallium ions for materials shaping and synthesis. Ga droplet-free milling in the semiconductor materials GaAs, GaP and GaN can be achieved by substituting the traditional Ga+ ion source with an Au+ ion source. In addition to droplet free features, the milling rate is increased to speed up processing and increase yield. Au+ and Si+ implanted ions have been shown to assist in graphene formation in SiC at a lower temperature while implanted Ga+ ions have not provided the same result. As focused ion beam processes continue to further impact in fabrication methods, the migration away from Ga and towards alloy metals for ion sources is an obvious evolution.

REFERENCES

BIography
Brent Gila has a PhD (2000) in materials science and engineering from the University of Florida (UF). Since 2002 he has been a research scientist at UF and has worked in the fields of gate dielectrics for wide bandgap semiconductors, nitride semiconductor devices, solid state sensors, graphene fabrication and advanced materials processing. In 2008 he joined the Nanoscale Research Facility at UF as a staff scientist and has aided with the facility planning and operations and assisted with the development of non-gallium focused ion beam lithography. In 2011, he became the Director of the Nanoscale Research Facility.

ABSTRACT
We have investigated unique ion beams for materials modification applications. The dedicated multiple-species focused ion beam nanofabrication instrument provides down to sub-10 nm beams with exceptional stability from a single ion source. Applications range from fundamental machining studies of III-V semiconductors to surface functionalization for selective growth of graphene.

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