Appendix E

PRELIMINARY HIGH CONTRAST GRATING FABRICATION

High contrast grating fabrication was attempted in two material systems. Amorphous Si and GaP layers were patterned by ebeam lithography and etched by ICP-RIE etching. Procedures, results, and discussion of remaining work is presented below. The a-Si material was deposited by PECVD directly onto a SiO_2 slide while GaP was deposited via MOCVD onto Si. The layer was wafer-bonded onto a SiO_2 slide using SU-8 and the Si etched away by XeF_2. Process development of this lift-off procedure and more detailed results are described in Hal Emmer's thesis. A Leica Microsystems EBPG-5000+ was used for electron beam lithography and a Oxford Instruments System 100 ICP 380 for ICP-RIE etching.

GaP Patterning

1. Clean the surface of the GaP layer, e.g. rinse and sonicate in acetone and IPA and dry on a hotplate
2. Spin on resist according to manufacturer's specification (30 s, 3000 repm for ma-N 2403 and prebake 90°C for 60 s)
3. Thermally evaporate ~5 nm Al layer.
4. Pattern via ebeam lithography.
5. Develop resist (base developer, e.g. mf-319, which is a TMAH solution, so it also removed the Al layer)
6. ICP-RIE etch (a functional but not optimized recipe for n-doped 100 and intrinsic 112 oriented GaP films: 30 sccm Ar, 5 sccm Cl, 2000 W ICP, 50 W forward power
7. Remove remaining resist if needed

a-Si Patterning

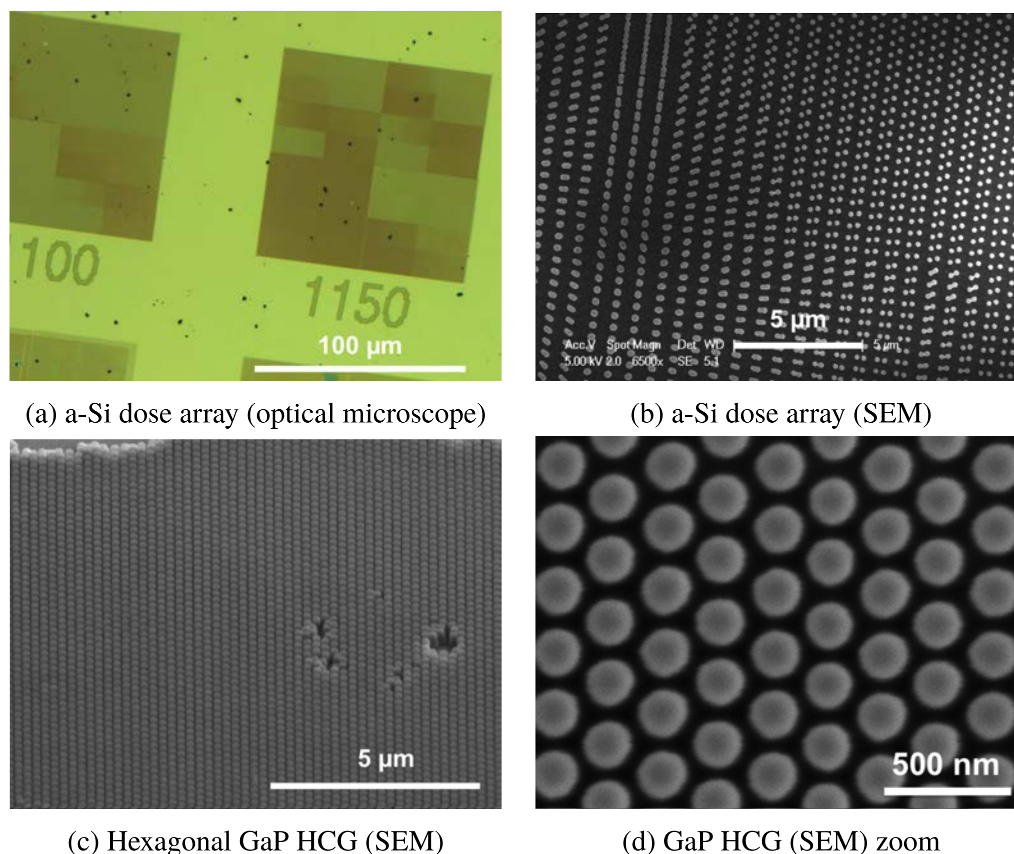
1. Clean the surface of the a-Si layer
2. Spin on resist (e.g. 950 A2 PMMA)

3. Deposit ~5 nm Al layer
4. Pattern via ebeam lithography.
5. Develop resist (MIBK-IPA followed by IPA dunk to stop development). A quick O_2 plasma (~5 s) serves to clear residue.
6. Deposit alumina etch mask (used 15 nm for ~300 nm etch depth)
7. Remove remaining resist
8. ICP-RIE etch using a pseudo-Bosch etch (SF_6/C_4F_8 - see Mike Henry's thesis for details)

Results

A couple of a-Si gratings and a single GaP dose array were prepared. The a-Si gratings were all patterned by ebeam lithography without an aluminum charge dissipation layer. This caused charge build-up during exposure which led to beam deflection during the pattern writing. The results of this are shown in Figures E.1a and E.1a. The optical image shows a patchwork of domains. Zooming in closer by SEM shows that what should be a hexagonal grating has many distortions including nearest neighbor grating elements subsumed into a single grating element in the bottom left to dimer patterns elsewhere. In contrast, the bottom two images of Figure E.1 shows a uniform hexagonal GaP grating. For the latter sample, a 5 nm Al layer was thermally evaporated on top of the resist to dissipate the charge. (The Al was thermally deposited to avoid exposing the ma-N resist which is also a UV-curable resist with the stray radiation an ebeam evaporation step would produce.) This prevented the beam deflection and resulted in a significantly more accurate ebeam lithography writing step.

Two sets of SEM images were taken to assess the GaP RIE etch. The recipe was recommended for etching n-type 100 GaP, but the film I used was an intrinsic 112 layer. A dose array was made, and one patch (15 nA beam, 1250 $\mu C/cm^2$ dose) was imaged in depth. As shown in Figure E.2a, a large defect was present in one of the dose array segments. Pillars at the edge of this defect were measured (Figure E.2b). Additionally, an *in-situ* Pt deposition and FIB cross-section milling were done at the center of the grating. In both regions, the etch seems to have resulted in pillars with fairly straight side walls. At the defect edge, the etch seems to have got fully through the GaP layer and into the SU-8 as seen in the ridge toward the bottom of



(a) a-Si dose array (optical microscope)

(b) a-Si dose array (SEM)

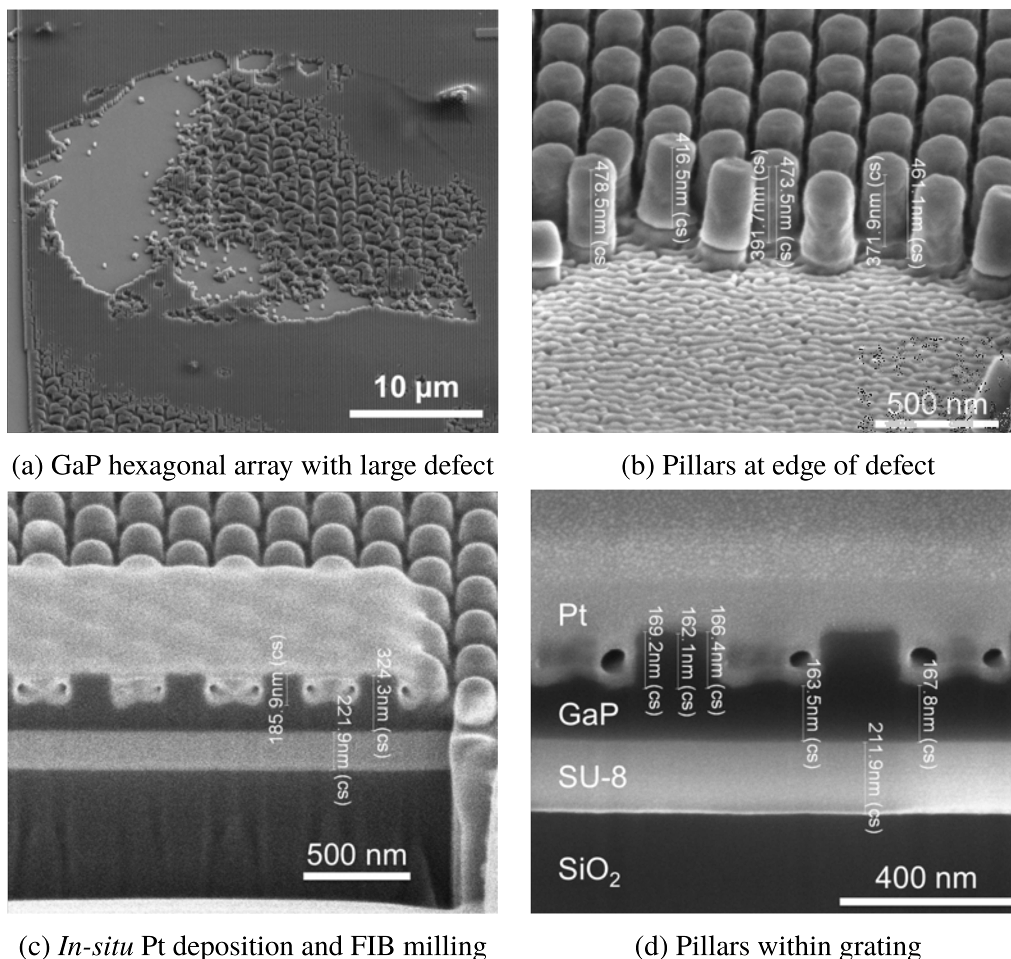
(c) Hexagonal GaP HCG (SEM)

(d) GaP HCG (SEM) zoom

Figure E.1: (top) Pattern drift in what should be a hexagonal grating due to charge build-up during ebeam lithography of a-Si film on quartz; (bottom) GaP grating patterned through 5 nm Al without pattern drift.

the pillars in Figure E.2b. In contrast, in the more central portion of the grating, the GaP film seems to be etched only part of the way through and the total thickness seems to be less than at the defect edge.

There are many possible regions for the mismatch between the etch results at the defect edge and in the middle of the grating. It is possible the GaP film itself had thickness variations. However, such a ~100 nm variation in a 400 nm films within 100 µm seems unlikely given that the 1 cm by 1 cm film visually appears quite uniform. It is also possible that the ma-N resist thickness varied. The sample geometry was not optimal for uniform spin coating. The SiO_2 substrate 2.5 cm by 2.5 cm with the 1 cm by 1 cm GaP film transferred onto it. This was then cross-sectioned, and the smaller of the two resulting pieces was used for the dose array. The SiO_2 substrate was rectangular, and the GaP film was not centered on the substrate. In addition, there was a ring of SU-8 around the edge of the film. In fact, I attempted to measure the thickness of the GaP layer by profilometry. However,



(a) GaP hexagonal array with large defect

(b) Pillars at edge of defect

(c) *In-situ* Pt deposition and FIB milling

(d) Pillars within grating

Figure E.2: While the GaP at the edge of the defect (a) appears to be etched fully through the GaP layer (b), the GaP away from the defect in the bulk of the layer appears only partially etched.

during the wafer bonding process, excess SU-8 from between the GaP, and the SiO_2 substrate leaked out forming a ring around the GaP which was 1-2 orders of magnitude taller than the GaP layer. All of this lends itself to uneven spin-coating of the resist on the sample. Thus in the bulk region if the ma-N thickness was lower, it is possible that the resist was etched through faster, removing material from the top of the pillars during the etch and accounting for the smaller overall thickness. Given the dense packing of the grating elements, it is possible that there was more restricted gas flow during the etch in bulk regions of the grating rather than near the defect edge, giving a high etch rate at the defect edge. These accumulated uncertainties underscore the need for characterization between each processing step to identify the source of such issues. Thus attempts to measure the GaP thickness by profilometry led to the stylus moving the whole sample rather than moving across

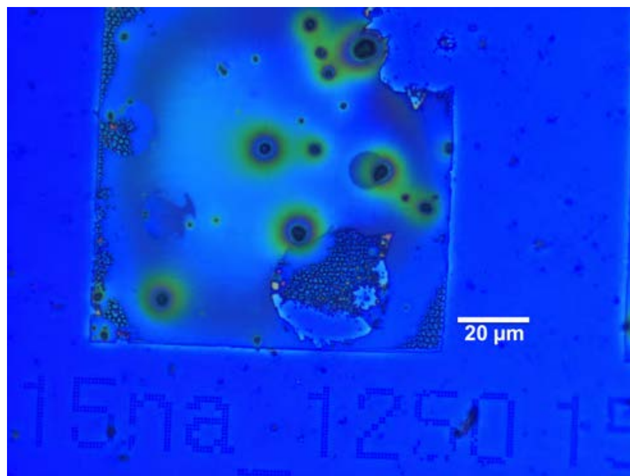


Figure E.3: Optical microscope image of one pattern in GaP dose array showing many defects in the array as well as many particles or dust specs around the grating.

the sample even with the sample vacuum on. Records from Chris Chen and Rebecca Saive who grew the layer suggested it was around 200 nm. SEM measurements after patterning and etching, however, suggested a thickness closer to 400 nm.

Another remaining concern to be addressed in future HCG fabrication is better cleaning of the semiconductor layer before processing. Figure **??** shows many defects in the grating as well as particles strewn across the surrounding area. Other cleaning options include plasma ashing followed by an oxide etch. If the defects are due to the presence of particles, this will be a problem for large scale uniformity. An additional possible source of defects within the grating is the high dose. The recommended amount for ma-N 2403 is closer to a few hundred $\mu C/cm^2$. It is possible that over-exposure caused the resist to bubble, forming some of the defects. Finally, the dust could be embedded in the SU-8 film between the GaP and the SiO_2 substrate.

Attempts at repeating the patterning at a larger scale in the other half of the same GaP cross-sectioned film failed at the patterning step. The developed resist showed no pattern. Possible reasons for this failure include little or no resist stuck to the GaP film in the initial spin-coating step, the Al layer was too thick for the exposure to go through the whole resist layer, the Al evaporation step somehow developed the whole resist layer, and that the film was overdeveloped. The only difference I know of between the first and second sample was that the second had an additional cleaning step of ultrasonication in acetone. The ultrasonication also caused some flaking off of GaP film material. It is however possible that some additional treatment was

applied to one half of sample before it was give to me, e.g. some sort of surface treatment that would affect the adhesion of ma-N.

Future work in fabricating high-contrast gratings requires optimization of film cleaning, uniformity of the spun-coat resist layer, and optimization of the etch conditions.

Tips

Some stray pieces of accumulated wisdom from the many folks who trained me in lab:

- Start the fabrication process with a dose array straddling the suggested dose range for the resist to select optimal value. Generally, a smaller beam current gives more precision, but a longer exposure is required to achieve the target dose (in Coulombs/area), so the exposure is slower.
- Prepare beakers with all needed baths ahead of time for wet chemical processes, e.g. set up beakers for development and rinses to follow the developer, especially if the development time is sensitive.
- Confirm via optical microscopy that each step has been successful.
- It is hard to find a 50 µm x 50 µm pattern on a 1 cm^2 sample so large noticeable markers are very useful for locating patterns for any characterization or measurement after fabrication, e.g. a thick large box or thick text markers written with a low resolution beam (e.g. 50 na or 100 na beam).
- Dose arrays need to be just large enough to image to ensure that the process has gone well. If not doing proximity corrections about 100 µm x 100 µm is large enough to provide an interior region that is not experiencing edge proximity effects. With proximity corrections even smaller is possible.
- Scribing an ’F’ or other non-mirror symmetric symbol on a wafer can help identify if the correct side is up on a transparent substrate with a transparent thin film on it.