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6. AUTHOR(S)
Dr Falco

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
University of Arizona
PO Box 3308
Tucson AZ 85722-3308

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Final Report for
"Atomic Lithography: Forcing Epitaxial Growth Using X-ray Standing Waves"
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6 November, 2002

Charles M. Falco
Optical Sciences Center
The University of Arizona, Tucson 85721-0077

I. Introduction

Over the last year we made considerable progress towards demonstrating an effect of an x-ray standing wave on the deposition of a Ge film. In the presence of the standing wave we observed a change in the film morphology of Ge grown on Si(111) below the temperature needed for epitaxial growth. Beam-exposed regions appear flat and resemble the Si(111) substrate, while unexposed regions are rough and display polycrystalline morphology similar to that seen for Ge growth on amorphous substrates. Consistent with our expectations, at higher deposition temperatures the effect is no longer observable. Similarly, for the deposition conditions we have been able to investigate to date on amorphous substrates we do not see any difference in the morphology between beam-on and beam-off regions. This is consistent with an effect arising from a weak coupling between the standing wave field and the Ge atoms on the surface which, at the x-ray intensities we can achieve without modifications to our optical geometry, is insufficient to modify the growth by itself, but when coupled with the periodic potential due to the substrate can push the Ge atoms into a new stable configuration. We find this to be very promising development toward our ultimate goal of atomic lithography. Below, we discuss in more detail the experimental approach to these recent standing wave depositions and their results.

II. Experimental Details

Our approach to the generation of an x-ray standing wave was to use the interference of an incident and reflected beam from a suitable x-ray reflector. Depending on the x-ray reflector used, this technique generates a standing wave in a region 250–500 μm from the surface of the reflector, with a periodicity that is characteristic of the reflection and nodes parallel to the surface. The experimental challenges to using this technique are positioning the reflector such that the standing wave exists at the substrate surface, and aligning it in vacuum with sufficient precision to ensure that the intensity of the standing wave is optimized.

We addressed these challenges using the experimental geometry shown in Fig. 1. We placed the reflector directly in contact with the substrate such that the reflecting surface is perpendicular to the surface on which deposition will take place. This ensures that the orientation of the standing wave nodes is correct and that the standing wave extends to the substrate surface. As shown in Fig. 2, the sample is mounted on a rotation stage such that the angle of incidence Θ can be continuously scanned from 0–90°. In addition, a Si-PIN photodiode x-ray detector is mounted on a separate rotational feedthrough such that the detector angle (shown in the Figure as 2Θ) can be varied independently of Θ if desired. The detector faces the sample through a 1 mm pinhole to

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monitor the reflected intensity. Combined with the azimuthal sample rotation available on the sample holder, this creates an in-vacuum Θ–2Θ Bragg-Brentano diffractometer which we can use to align the standing wave generating crystal to the (111) reflection. With these two degrees of freedom, we are able to align the reflector quite accurately with respect to the incident beam, and ensure that significant intensity is in the reflected beam.

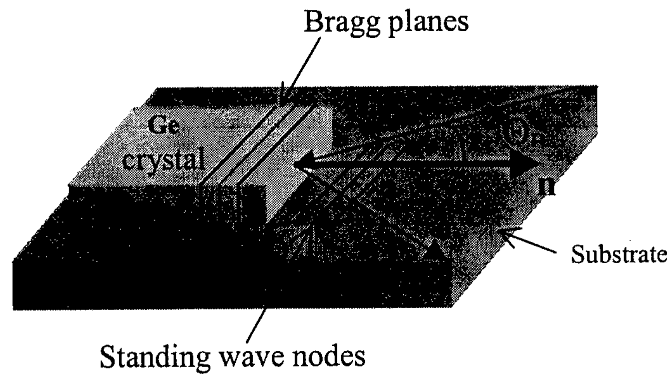

Figure 1. Experimental geometry for the x-ray standing wave deposition experiments. The x-ray beam is parallel to the substrate surface, and incident on the Ge generating crystal at the Bragg angle. This results in the standing wave nodes as shown by the blue lines.

The x-ray source is a Rigaku 18 kW rotating anode tube with a Cu target, operated at the unit's maximum available power (60 kV, 300 mA) during deposition. To select the Cu-Ka radiation, and to further increase the standing wave intensity, we use a Si bent-crystal, Johannson-type focusing monochromator with the focus set at the sample position. To achieve optimal alignment of the reflector, we first set the detector at the maximum of the straight-through beam with the sample moved out of the away. We then scan the sample in the direction perpendicular to the beam to locate the position at which the reflecting surface of the mirror blocks half the intensity. At this position, we then scan the sample azimuth to locate the angular position where the mirror is parallel to the beam. Starting from this position, we then set the sample azimuth at the expected position of the reflection we want to use for the standing wave, and scan the detector angle to find the reflection. Using this procedure we are always able to find an intense reflection where we expect it.

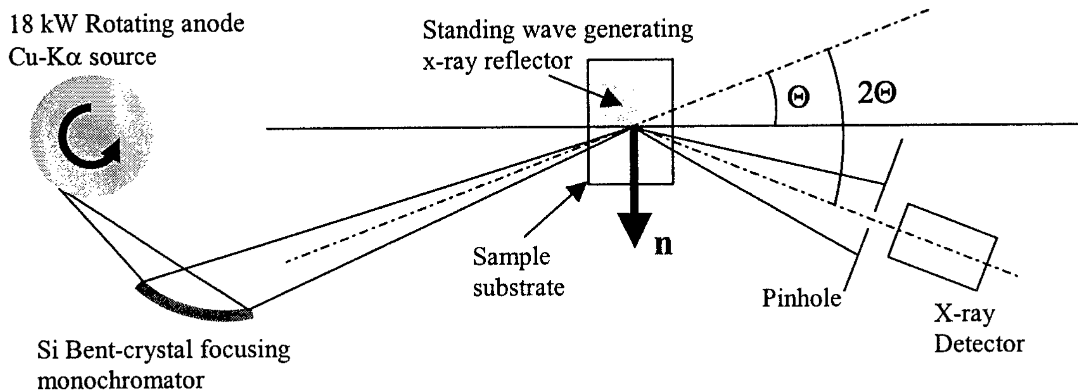

Figure 2. Beamline geometry used for our standing wave experiments. The sample and detector can be rotated independently about the focal point of the monochromator, as well as form a Θ–2Θ diffractometer for aligning the x-ray reflector.

For most of the experiments described in this report, we wanted a standing wave with the periodicity of the atomic spacing of Ge. To achieve this, as our reflector we used a Ge(111) single crystal specially cut and polished so that the (111) reflecting face is perpendicular to the substrate surface (in the **n** direction indicated in Figs. 1 & 2). Then, by aligning the incidence angle to the (111) Bragg reflection, we obtained a standing wave with periodicity identical to the 3.26 Å distance between reflecting planes. In this geometry, we estimate the spatial extent of this standing wave to be ~250 μm from the Ge crystal. Using a Ge(111) crystal as the reflector, we typically obtain a maximum count rate in the Bragg reflection of ~8% of the incident beam intensity, indicating that this standing wave exists with significant intensity. In addition, some of our recent experiments involved a longer period standing wave in which we used the low angle finite size reflections from thin Au films grown on glass. In these experiments, we usually obtained about 4% of the incident beam intensity in the reflected beam.

We characterized all of the films grown in our experiments using *in situ* reflection high-energy electron diffraction (RHEED) and scanning tunneling microscopy (STM). Although RHEED was used to determine the polycrystalline or epitaxial nature of the out-of-beam regions, reliable positioning of the RHEED beam precisely on the very small in-beam regions was problematic with our current setup so below we do not compare RHEED results between beam-on and beam-off regions. Using a special bent STM tip, as shown in Fig. 3, we are able to obtain micrographs from as close as 5 μm from the surface of the x-ray reflector; we can also access points up to several mm away. This allows us to reliably obtain and compare beam-on and beam-off images from the same sample simply by moving the tip out of the expected spatial extent of the standing wave. This is accomplished by approaching the Ge crystal with the tip using the coarse lateral motion of the scanner stage until a tunnel current is observed. This sets the d=0 point. We then back off by ~5μm and perform the usual approach to the Si substrate. Although using these longer, bent tips may introduce some additional noise into the tunnel current signal, straight tips would limit our approach to d=135 μm due to the radius of the W wire used to make the tips.

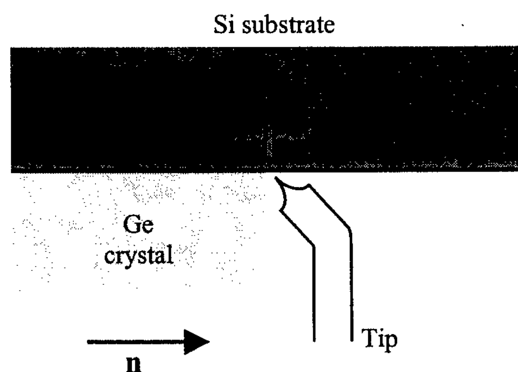

Figure 3. Bent-tip geometry for obtaining STM micrographs from the beam-exposed regions of the films. Using this technique we are able to take micrographs within d=5 μm of the Ge crystal.

We made standing wave depositions on both amorphous and crystalline substrates at various temperatures. Prior to each deposition, the alignment was performed at low x-ray power with the sample at the deposition temperature to reduce the possibility of thermal drift in the sample angular position. We then increased the x-ray power to the maximum obtainable from the rotating anode source for the deposition. Ge was deposited from effusion cells at 1200 °C. The deposition rate at this temperature was calibrated using *ex situ* low angle x-ray reflectivity from ~100 Å thick Ge films grown on Si wafers. The rate obtained was 1.8 Å/min. We first attempted epitaxial growth on

amorphous oxidized SiO_2 wafers using the standing wave from the (111) Bragg reflection of the Ge crystal. Following this, we systematically mapped out the phase diagram for the growth of Ge(111) on Si(111) with and without the standing wave. Finally, some attempts were made at patterning of films using the long-period standing wave obtained from low-angle reflections.

III. Results

Following the successful alignment of the standing wave generation beamline, we began a series of Ge depositions designed to detect a modification of the growth mode resulting from a coupling of the flux with the standing wave radiation field. Our first efforts centered on room temperature grown 20 Å films on oxidized Si wafers. *In situ* STM examinations of the in-beam and out-of-beam regions showed polycrystalline Ge with an approximate grain size of 50–70 Å in both cases. No difference in morphology or crystallinity was observed between the beam-on and beam-off samples. Attempts at patterning Ge growth on SiO_2 using long-wavelength standing waves were also unsuccessful. This shows that the coupling of the Ge atoms to the standing wave is insufficient to force epitaxial growth, or even modify the growth, of Ge on amorphous SiO_2 under these particular conditions. The two most likely causes for this are insufficient x-ray intensity and excessive thermal energy of the Ge flux atoms. The adatoms are rapidly quenched from the 1200 °C evaporation temperature by the surface upon incidence, and are exposed to the standing wave for up to 60 s before they are buried. However, even at room temperature sufficient thermal diffusion may exist to overcome the standing wave effect. Therefore, it appears that for our experiments to date on the deposition on amorphous substrates we have been too far away from the epitaxy conditions to force the system into crystalline growth using the standing wave effect from our rotating anode source.

In order to increase the chance of detecting this small standing-wave effect, we moved the conditions closer to those required for epitaxy and looked for any small modifications of the growth due to the standing wave. To this end, we performed a series of depositions on crystalline substrates close to, but below, the substrate temperature needed for crystalline Ge growth. We used non-miscut Si(111) wafers, etched in 2% HF and annealed under vacuum at 750 °C to remove the natural SiO_2 layer.

In Fig. 5, we show micrographs taken from the beam-on and beam-off regions of 30 Å Ge films grown on Si(111) at 80 °C. The region exposed to the beam during deposition (a) appears very flat. Note that the surface exhibits 30 Å high bumps that show up as the yellow features in this false-color image. We have previously found that these bumps are present on bare Si(111) even after the in-vacuum anneal, so they are not related to the Ge deposition. In the regions between the bumps we see a very slight mottling of the surface indicating that the surface is not bare Si, which would be atomically flat. Since the Ge film has not covered the 30 Å features on the Si surface, it may be thinner in this region. This suggests that the x-ray standing wave may inhibit the deposition, possibly due to ionization of some of the flux. However, we note that *ex situ* optical microscopy on these samples did not reveal any change in the appearance or reflectivity of the film in the beam-on region, as would be expected if the thickness were significantly different. Also, we did not observe any inhibition of deposition due to the beam for the film grown on amorphous substrates.

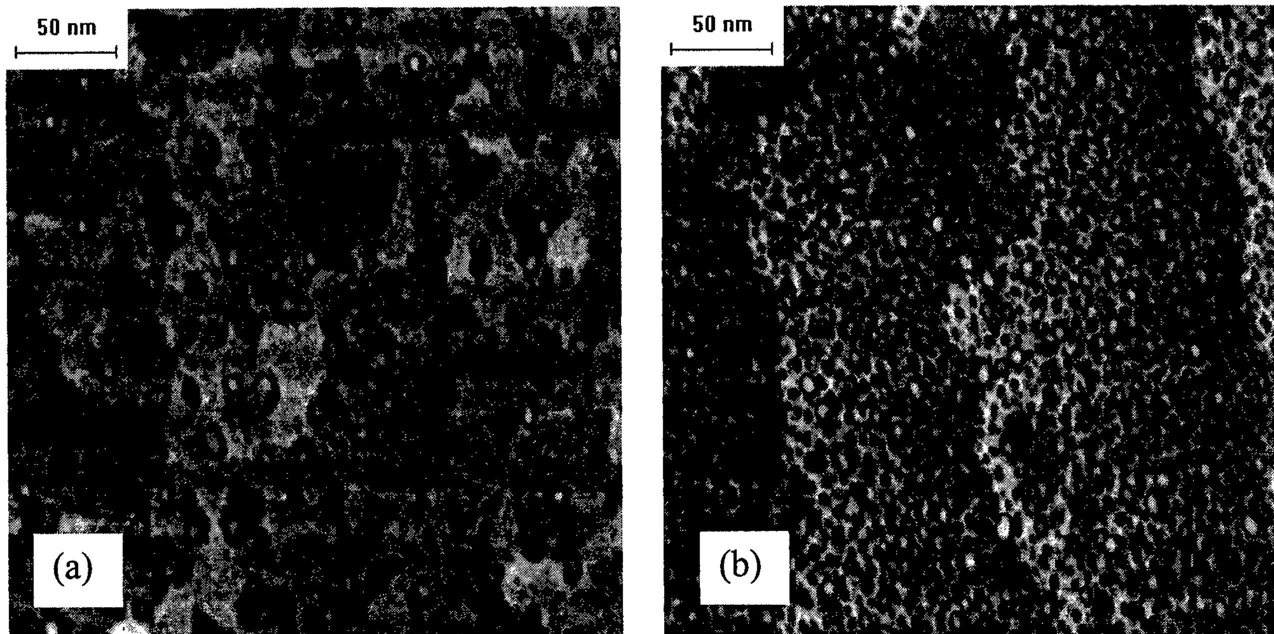

Figure 5: STM micrographs taken from a 30 Å Ge film grown on Si(111) at 80 °C with a 3.26 Å period x-ray standing wave (a) and without (b). The yellow bumps in the false color image are associated with the Si (111) substrate, and not the Ge film.

In the beam-off region (b), the morphology is very different. We see the same 30 Å bumps as in the beam-on sample and bare Si, but the regions between them are now filled with individual crystallites, with increased roughness. The transition between these two morphologies occurs abruptly between 200 and 250 μm away from the Ge standing wave generating crystal, which is consistent with our estimates of the spatial extent of the standing wave. Therefore, this strongly suggests that the standing wave modifies the growth of Ge on Si in the temperature regime below that required for epitaxial growth, resulting in a smoother film.

At 150 °C deposition (Fig. 6) the differences in the morphology are more subtle, with polycrystalline Ge existing over a modified morphology. Above 150 °C, we see no differences between the beam-on and beam-off regions, and RHEED indicates that the films are epitaxial at 175 °C and above.

IV. Discussion

The results noted above suggest that the x-ray standing wave does produce a potentially useful modification of the growth mode of the Ge. The exact nature of the interaction is still unknown, and is the subject of some of the proposed future experiments detailed in a forthcoming White Paper. We note, however, that at the growth parameters and standing wave geometry we are using, the Ge atoms spend only about 10^{-6} s passing through the standing wave on the way to the substrate, versus about 60 s diffusing over the surface before they are covered. Therefore, it is likely that the greatest effect on the adatoms occurs during the diffusion over the surface under the influence of both the standing wave and substrate potentials. The effect we observe appears to require the presence of *both* the standing wave and a Si(111) template on the surface. In other words, deposition on the amorphous substrate in the beam results in rough polycrystalline growth, as does deposition out of the beam on crystalline Si(111). This suggests that the

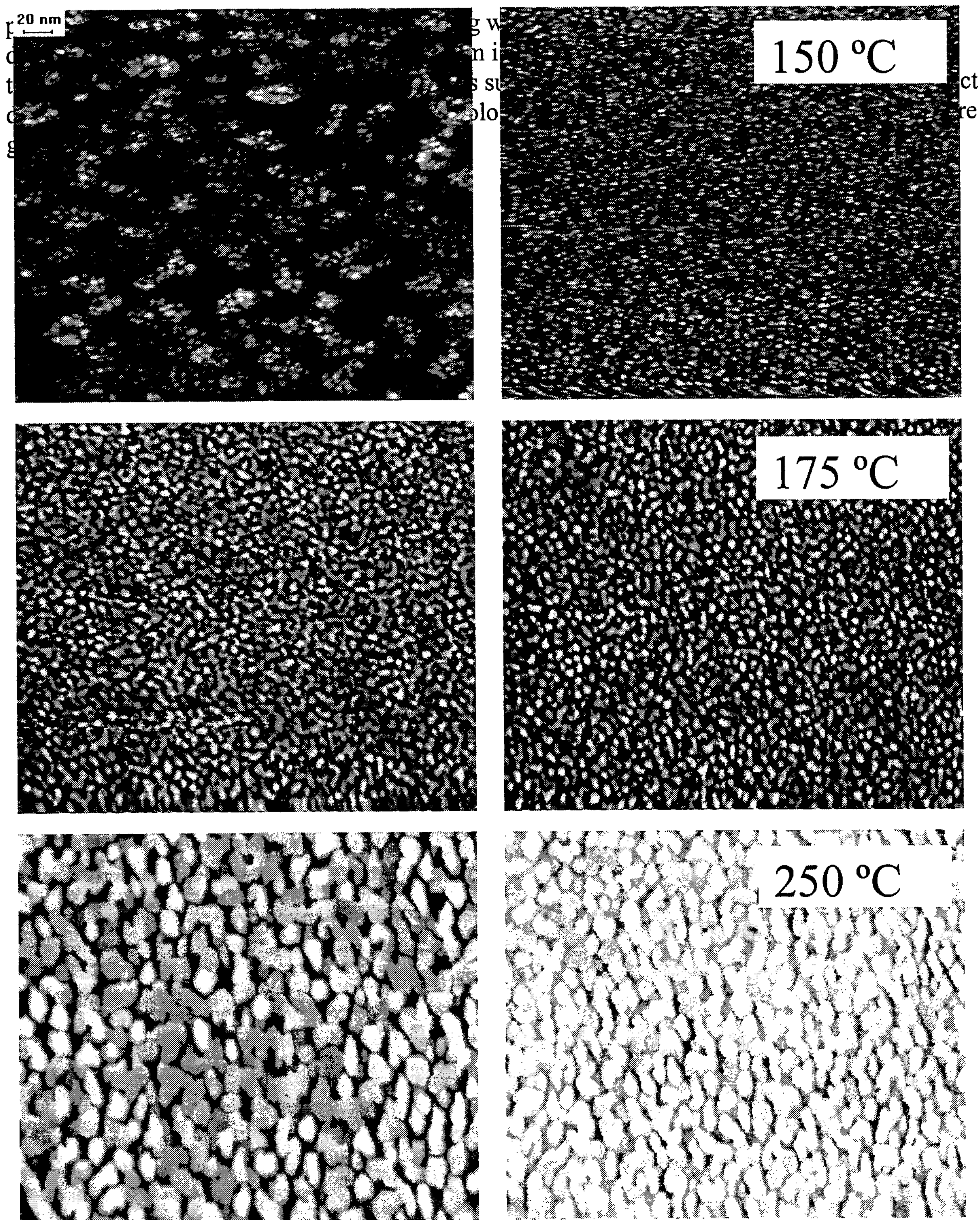

Figure 6. STM micrographs from 30 Å Ge films grown on Si(111) at various substrate temperatures with a 3.26 Å period x-ray standing (left column) and without (right column). RHEED indicated that the film grown at 250 °C is epitaxial, and the lower temperature ones are polycrystalline.

The results reported above are certainly very suggestive. However, although our experiments have now ruled out most potential spurious effects, a few subtle ones remain to be investigated. In our earlier non-standing wave experiments, we considered the possibility of a thermal effect due to heating by the x-ray beam, and estimated the temperature change from x-ray absorption to be very small. The experimental geometry we are now using for our experiments does raise the possibility of other thermal effects. We planned several final experiments during the present grant for September 2001 to test for such spurious effects. Unfortunately, problems with our sample heater and the AFM/STM have prevented us from completing them. These experiments would be the first priority if a follow-on proposal were funded by AFOSR. One concern we need to eliminate is the possibility that placing the x-ray reflector in contact with the substrate might create a thermal gradient close to the reflector. If this were the case, and if the growth morphology turns out to be strongly affected by the growth temperature, the region close to the reflector could appear different from the region away from it. Depending on the sign of the temperature gradient, this effect could masquerade as an x-ray effect. We note that at 150 °C, the grains are slightly larger in the beam-on region, which would be possible if this region was slightly hotter than away from the crystal. However, this possibility could be conclusively tested with an experiment involving deposition of a Ge film with the Ge crystal in place, but with the x-ray beam off.

Another possibility is that the intense x-ray beam alone modifies either the flux or the substrate without the need for a standing wave. This could occur through ionization of the flux or adatoms on the surface or through chemical modification of the substrate, thus altering the reactivity of the adatoms and surface, and consequently the sticking coefficient or the surface diffusion rate. It is not clear whether this possibility is consistent with our results, as it can depend on the details of the surface conditions or trace contaminants, what residual gases may be present, and probably other uncontrolled factors. However, we can test this possibility simply by deposition of a Ge film with the x-ray beam on, but misaligned from the Bragg angle.

V. Proposed Future Work

If a follow-on proposal were funded by AFOSR, our first priority would be to complete the verification experiments noted above to conclusively determine if the effect shown in Fig. 5 is actually due the standing wave, or due to a spurious effect. Following that verification, and depending on the results of those experiments, there are several studies that we would next pursue. We have designed these experiments in consideration of the fact that the effect we see with Ge is fairly weak. By relaxing some of the constraints that exist in the Ge depositions, we hope to demonstrate a stronger effect.

First, more long wavelength standing wave depositions would be very useful in helping us categorize the effects of various parameters. Although we found no effect in the attempts reported here, we only deposited on amorphous SiO_2 substrates (a substrate on which we did not see any effect of the standing wave) at one standing-wave wavelength. A more systematic study is needed. In particular, depositions on etched Si(111) wafers would go a long way towards determining if the effect is due to the standing wave. For example, if we can modulate the

morphology between that of Figs. 5a and 5b with a periodicity equal to that expect for a given reflection geometry, that would conclusively demonstrate the standing wave effect.

Second, our experiments so far have been limited by the fact that we have only one photon energy available in our lab (Cu-K_α), and that we have been interested in depositing Ge or Si on amorphous substrates. This effectively sets the detuning factor from resonance between the radiation field and the incident atoms at a fairly large value, and does not allow us to vary it in order to optimize the coupling between the radiation field and the adatoms. Further experiments at different detuning factors have very good potential for demonstrating a stronger effect. The detuning factor can be modified either by changing the incident radiation energy or by changing the atomic species of the adatoms. Our approach would be the latter, since modifying the radiation energy requires a separate target for each energy used, which is costly. Therefore, we propose to repeat the experiments described in the results section using other deposition materials, such as Cu and other transition metals, to scan across a range of detuning factors. Although these are not semiconductors as planned in our original proposal, these experiments offer promise as a proof-of-concept, and would provide invaluable guidance for designing further experiments to increase the effect we have seen with Ge.

Finally, one obvious way to increase the effect is to simply increase the intensity of the incident radiation, and consequently the standing wave. We have done all of our experiments at the limit of our rotating anode source. However, it would be possible to gain a factor 2–2.5 by using a larger monochromator crystal. We note, though, that significantly higher intensities than that are available at synchrotrons, enabling positive results to be scaled up to true wafer-size areas . In addition, synchrotron radiation is tunable over a broad spectrum, making it possible to truly optimize the detuning factor. Therefore, once the proof-of-concept experiments described above are completed, it would be very useful in the longer term move the experiment to a suitable beamline facility, such as at the Advanced Photon Source (APS) at Argonne or the Advanced Light Source (ALS) at Berkeley. However, doing so would depend on the results of our depositions with different materials outlined above, as it would probably require success in these experiments to generate sufficient interest from a synchrotron group in order for them to allocate beam time.