

Scanning Tunneling Microscopy and Low Energy Electron Microscopy of Ir and Ag adsorbed on Ge(110) and Ge(111) Surfaces

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Abstract

The atomic behaviors of the surfaces Ge(111) and Ge(110) with adsorbents of Ag and Ir were examined through the techniques of Scanning Tunneling Microscopy (STM) and Low Energy Electron Microscopy (LEEM). LEEM analysis revealed the phase transitions of the Ge(111) surface as it was dosed with Ag up to a coverage of 1 monolayer (ML). Desorption of Ag from the surface was observed upon subsequent heating. STM images at approximately 0.5 ML of adsorbent revealed the coexistence of three phases: $c(2 \times 8)$, (3×1) , and (4×4) . STM images of Ir on Ge(111) revealed competing hexagonal and square lattice structures for the germanium, as well as the growth characteristics and mode of the iridium. Finally, LEEM analysis revealed the method of growth of Ag on the surface Ge(110). The adsorbent was found to organize on the substrate in parallel lines which varied in thickness and length according to the dosing temperature. An additional phase transition for the substrate was found at 406°C.

1 Introduction

Surfaces often exhibit different structural behavior from that of the bulk of the material due to the different distribution of forces among the atoms, complicating the problem of obtaining precise descriptions of them. However, such understanding—in addition to satisfying intellectual curiosity—is progressively growing in importance for industries such as electronics, where devices are becoming increasingly smaller, ever raising the proportion of surface area to volume.[1] Scanning Tunneling Microscopy (STM) and Low Energy Electron Microscopy (LEEM) are two means for experimentally determining surface structure and behavior. These microscopes were used to study the surface behavior of Ge(111) and Ge(110) with adsorbents of Ag and Ir, materials representative of the metal-on-semiconductor interfaces important to the electronics industries.

1.1 Surface Behavior

1.1.1 Phases of Surfaces

The configuration of the atoms on the surface of a clean sample will not necessarily be the same as that of the atoms which lie in the planes parallel to the surface but within the sample. Because atoms on the

surface have no bonds to atoms above them, the minimization of free energy of the surface atoms can result in a restructuring of the surface. For the Ge(111) surface, the surface structure is $c(2 \times 8)$ [2], a name given in relation to the basic two-dimensional hexagonal lattice. (See Figure 1.)

When atoms from the metal are adsorbed onto the germanium surface, the structure of the surface may change again to keep the energy at a minimum. Such structural phase transitions may occur at particular temperatures and coverage of the adsorbent. The known phases of Ag on Ge(111) can be found in Figure 2.[3]

Transitions from one phase to another must either be first-order or second-order. A first-order transition occurs when there are distinct boundaries between the atoms in the original phase and the atoms that have changed phases. In a second order transition, the two phases do not coexist, but the sample undergoes one continuous change from its original phase to its new phase.[4] The two phases are indistinguishable at the critical temperature.

1.1.2 Growth on Substrate

The adsorbent may grow on the substrate in one of three ways.[5] If the adatoms grow in a layer-by-layer

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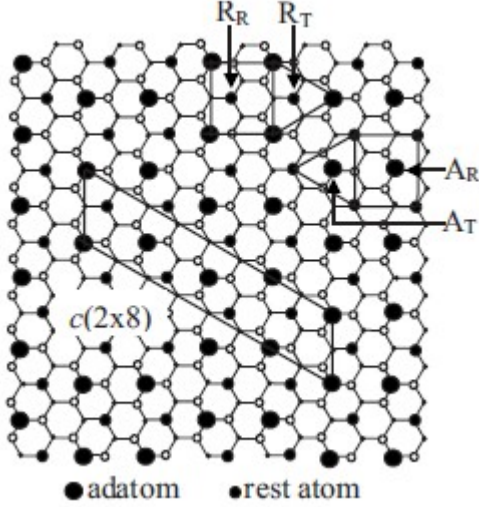


Figure 1: The vertical sides of the cell are 2 lattice widths apart, and the slanted sides are 8 lattice widths apart. The unit cell is has an atom at its center, thus making the structure $c(2 \times 8)$ in relation to the hexagonal lattice. Source: [2]

manner, they are exhibiting Frank-van der Merwe mode. On the other hand, if they bond to each other more strongly than the surface, then they form three-dimensional islands on top of the surface and their growth pattern is known as Volmer-Weber. A third mode of growth known as Stranski-Krastanov occurs when the atoms first form one even layer and then form islands on top of it.

1.2 Imaging Methods

1.2.1 Scanning Tunneling Microscopy

STM exploits the phenomenon of quantum tunneling to produce a small current between a sharp tip and the surface of the sample of interest. The tip is placed a few Angstroms away and a voltage difference is applied. A current due to quantum tunneling of the electrons I forms, and is related to the distance of the tip from the surface z by the relationship

$$I = Ve^{-A\sqrt{\phi}z}$$

where V is voltage applied, ϕ is the work function of the tip and sample, and A is a constant.[7] Because the current dies off exponentially in relation to an increase in distance from the surface, the tip can be scanned across the sample using a feedback loop such that the resulting current between the surface and tip remains constant. From the resulting motion of the tip, an image of the topography of the surface can be produced.[7] Resolution of 0.01 angstroms vertically and 2 angstroms laterally can be achieved. Us-

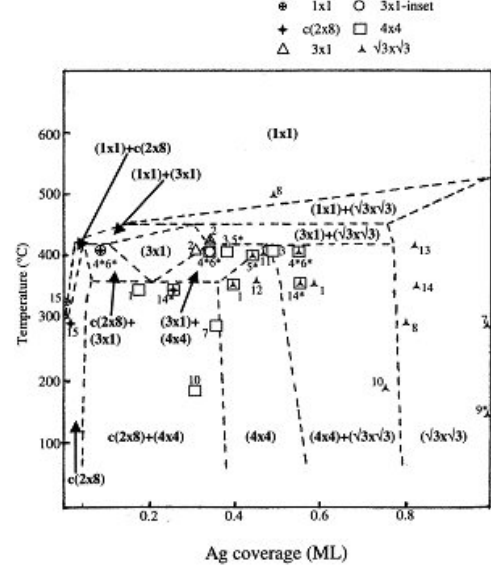


Figure 2: The known phases of Ag on Ge(111). Source: [3]

ing STM, the contrast between the substrate and the adsorbent layers are evident, as are any steps in the region. If the image is high enough in resolution, it is possible to determine the phase or phases coexisting on the surface of the sample.

1.2.2 Low Energy Electron Microscopy

The LEEM images the sample through detection of electrons backscattered off of the surface. Electrons are initially accelerated to high energy (20keV) in order to steer and focus the electron beam accurately. They travel through a series of lenses which focus them as a single beam on the sample. The objective lens focuses the electrons onto the sample and also decelerates them to energies of only a few electron volts in order to achieve surface sensitivity. The backscattered electrons are then accelerated again by the objective lens so that they can be steered further by magnetic lenses, directed into the imaging column, and focused to form the final image. (Figure 3.)

Differences in crystal orientation, surface structure, and the presence of adsorbed materials will cause a difference in the intensity of the beam[4], thus contrast will be seen between one phase and the other. The LEEM is capable of producing high resolution (down to 10nm) videos from the backscattered electrons[5], making it possible to observe the growth of the adsorbent on the surface. The mode of growth as well as the order of a phase transition can be observed due to the dynamic nature of this technique. The Low Energy Electron Diffraction pattern (LEED), yielding

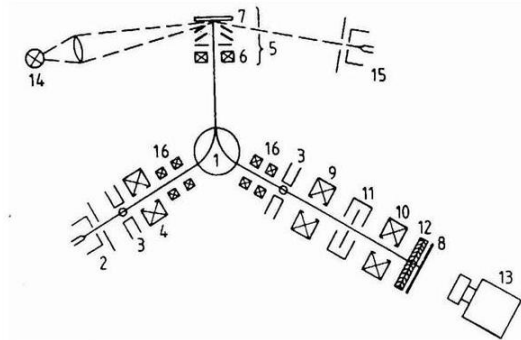


Figure 3: *LEEM Schematics.* (1) magnetic deflection field, (2) field emission electron gun, (3) quadrupoles, (4) beam forming lens, (5) cathode lens, (6) stigma lens, (7) specimen, (8) screen, (9) intermediate lens, (10) projector lens, (11) filter lens, (12) multichannel plates, (13) TV camera, (16) beam alignment coils. Source: [7]

the reciprocal space lattice, can also be viewed using the LEEM, offering another way to determine surface structure.

2 Experimental Procedures

2.1 Setup

The instrumentation consisted of a Low Energy Electron Microscope and a Scanning Tunneling Microscope which were connected by an analysis chamber. (see Figure 4.) In order to keep the sample clean for a time period long enough to make the measurements, experiments had to be run in Ultrahigh Vacuum (UHV), a pressure around 10^{-10} Torr, and transfer bars were used as well as a manipulator to move the sample from one instrument to the other without breaking vacuum. Three types of pumps were used to create and maintain vacuum: roughing pumps, turbo pumps, and ion pumps. The roughing and turbo pumps, however, were turned off during experiments to reduce vibrations.

Samples of Ge(111) and Ge(110) were cut from purchased wafers of those orientations. The samples were placed in Elmitec LEEM sample holders which had been modified to be compatible both with LEEM and STM. The holders contained tungsten filaments to facilitate heating as well as a thermocouple so that the temperature of the sample could be known.

The analysis chamber contained an argon ion sputtering gun for cleaning purposes. Samples, once introduced to vacuum, were first cleaned 16 times in the chamber by sputtering and annealing. This method

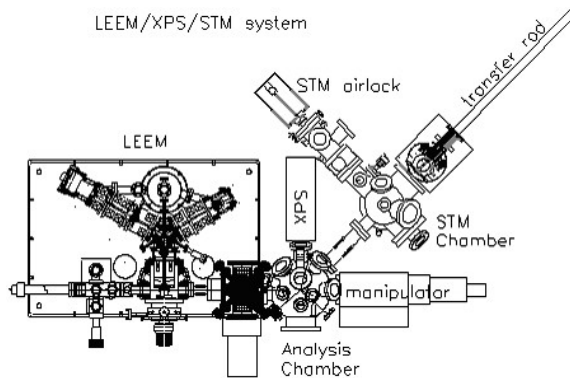


Figure 4: *UC Davis Advanced Surface Microscopy Facility schematic showing LEEM, Analysis Chamber, and STM.* Source: [8]

consisted of sputtering the sample with Ar^+ ions for 15 minutes to remove contaminants, followed by heating the sample at around $800^\circ C$ for 10 minutes to allow the surface to reorder itself. The final anneal typically was run for 30 minutes.

2.2 STM

The Ir and Ag dosers were located in the LEEM chamber, so samples used in STM experiments involving adsorbed metals had to be first transferred to the LEEM chamber for dosing. A calibration also had been run previously using the LEEM and a substrate-adsorbent pair with a known phase transition at 1ML to determine the dosing rate at a particular current. After the desired amount of adsorbent had been added, the sample was moved into the STM chamber and annealed at $500 - 700^\circ C$, then scanned after cooling.

The STM scanner was calibrated using a sample of clean germanium (see figure 5). The distance between germanium atoms was found to be a factor of 1.5 too large when compared to the predictions from literature values. All subsequent measurements were corrected to account for this.

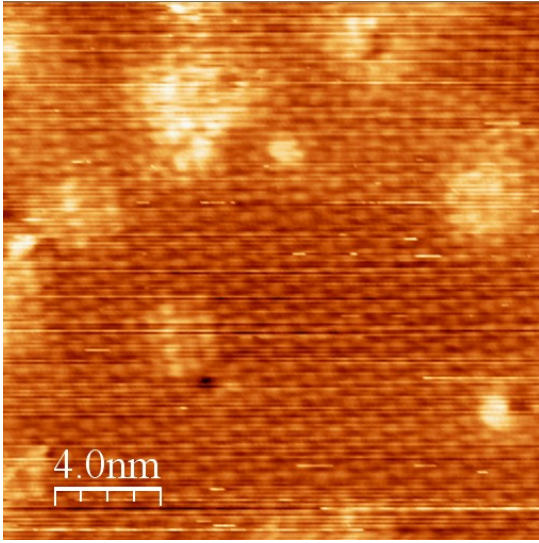


Figure 5: Clean $c(2 \times 8)$ germanium. Literature value for distance between close packed atoms is $2.45 \text{ \AA}$, so distance between two in $c(2 \times 8)$ should be approximately $5 \text{ \AA}$. Measured amount was 1.5 times that instead.

The images were later processed to make the features clearer, contrasts sharper, and flatten out the distortions using WSxM Scanning Probe Microscopy Software[9].

2.3 LEEM

Cleaned samples were first viewed in LEED and LEEM, making adjustments in lens focusing as appropriate. If the sample was sufficiently clean, it was then heated to the desired temperature for the experiment. Temperature was determined from a calibration curve created using optical pyrometer readings at several currents. (Figure 6) The desired amount of adsorbent was then dosed on the sample, using the previously determined dosage calibration. At the conclusion of most experiments, the sample was heated further until the adsorbent had desorbed off the substrate.

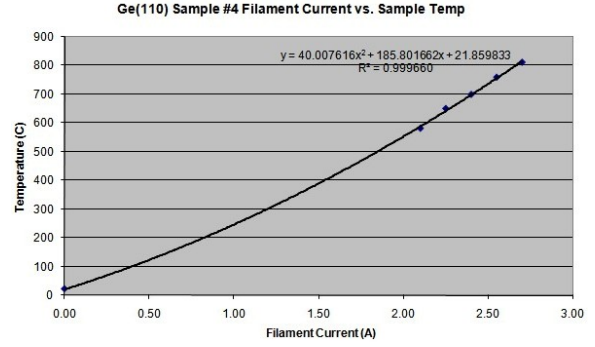


Figure 6: Calibration curve for Ge(110) sample used in LEEM experiments. Relates filament current to sample temperature.

3 Results

3.1 STM of Ag on Ge(111)

A Ge(111) surface was dosed with approximately 1/2 of a monolayer of Ag. The sample was then annealed at 450K for 5 minutes. From the image in Figure 7 it can be seen that the silver grows in triangular shaped domains as it covers the surface. The darkest and lightest triangular patches as well as the striated regions are Ag and the remaining sections are the germanium surface. Three phases can be seen coexisting in this region: $c(2 \times 8)$, (4×4) , and (3×1) .

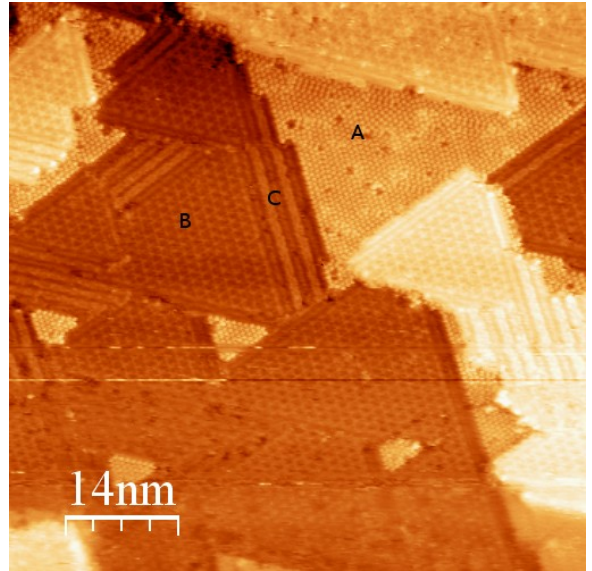


Figure 7: A: Germanium with competing $c(2 \times 8)$ and what appears to be a hexagonal domain. B: Ag with a (4×4) phase. C: Ag most likely in the (3×1) phase due to its single direction configuration. Also appears at phase boundaries, in agreement with the observations by Hammar et. al.

To verify that region A was indeed Ge in a $c(2 \times 8)$ phase, WSxM Scanning Probing Microscopy Software was used to measure the distance between the atoms going along a diagonal corresponding to the side of the $c(2 \times 8)$ unit cell (see figure 1).

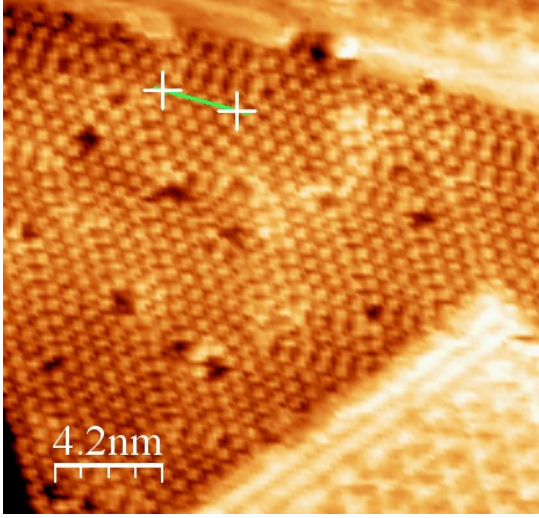


Figure 8: *An example of one of the portions averaged.*

After correction, the distance between the atoms in Figure 8 was found to consistently be 5 Angstroms, a number two times the close packed spacing of Ge, and thus consistent with the proposed $c(2 \times 8)$ phase. However, distortions in the structural phase also appeared to be present in the form of competing square (2×2) and hexagonal domains.

The measurements of the atomic spacing were also found for the suspected (4×4) region of silver adsorbent. The spacing between the large features was tested in several areas.

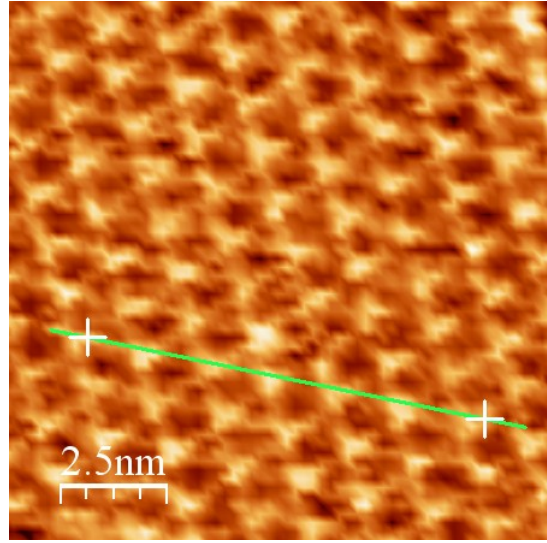


Figure 9: *An example of one of the regions measured.*

The distance between the features was found to be consistently 10 Angstroms, or 4 times the closepacked spacing of Ge, and thus consistent with the (4×4) phase.

3.2 STM of Ir on Ge(111)

About $1/2$ a monolayer of Ir was dosed on germanium. The sample had been annealed after dosing to 750K for 5 minutes. Figure 10 shows atomic resolution, but no iridium can be seen in the region. The surface is distorted from the added iridium adatoms, as there appear to be two competing domains: one hexagonal and the other square. The spacing between the atoms was found to be 5 Angstroms, suggesting that this germanium region was forming a square (2×2) surface.

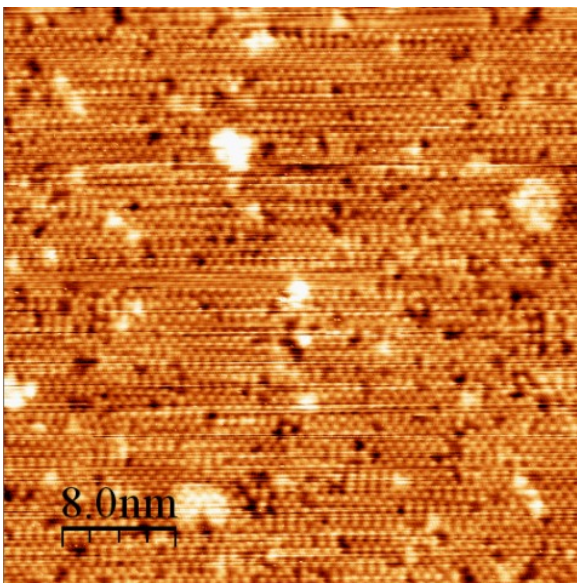


Figure 10: Germanium region. The white dots are image defects.

There appear to be two competing domains in this image: the square (2×2) domain and a hexagonal domain.

Though atomic resolution of the iridium has not been achieved to date, figures 11 and 12 of Ir on Ge(111) show the shape of the Ir domains as they grow to cover the surface.

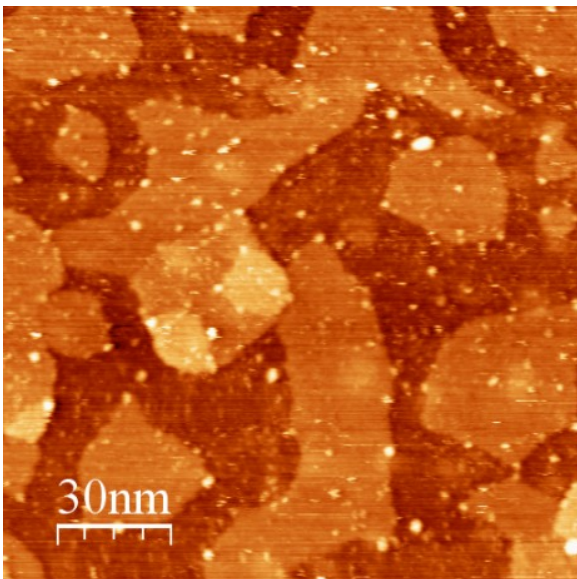


Figure 11: $1/2$ ML of Ir on germanium, annealed at 750K for 5 minutes. The lighter regions are iridium, while the darker region is germanium.

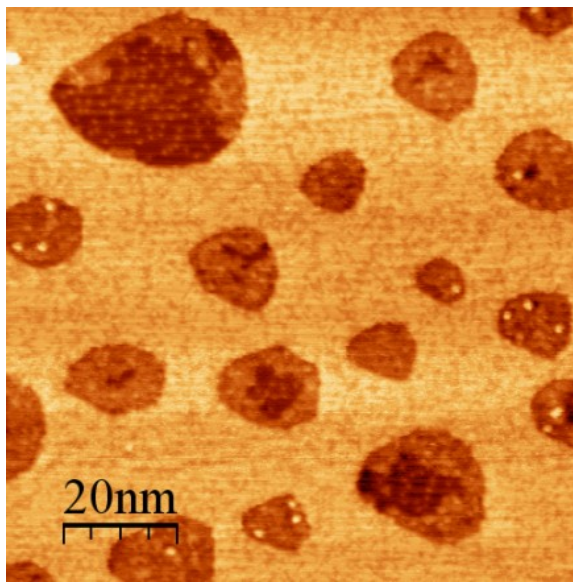


Figure 12: 1 ML of Ir on Germanium, annealed at 720K for 5 minutes. The darker regions are germanium, while the lighter region is iridium.

The patches on top of the iridium regions in figure 11 are most likely clumps of additional iridium, suggesting that Ir exhibits Stranski-Krastanov growth mode on Ge(111).

3.3 LEEM of Ag on Ge(111)

A sample of Ge(111) was heated to 250°C and then dosed with Ag up to 1 ML. The set of images in Figure 13 show the first phase transition that occurred.

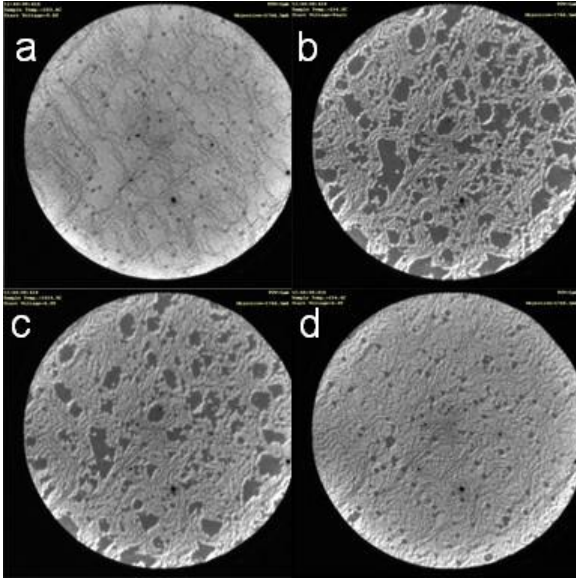


Figure 13: Phase transition of surface from a: $c(2 \times 8)$, to d: (4×4) . (a) clean $c(2 \times 8)$ surface. (b)→(d) the lighter surface is the (4×4) coming in and the darker surface is $c(2 \times 8)$.

Figure 13 shows the phase transition of the surface from $c(2 \times 8)$ to (4×4) as more silver was dosed onto the surface. The boundaries between the domains are clear as they coexist, so the phase transition is first-order. The domains are triangular, in agreement with the STM Ag on Ge(111) data.

As the amount of dosing reached 1 ML, a second phase transition occurred, shown in Figure 14.

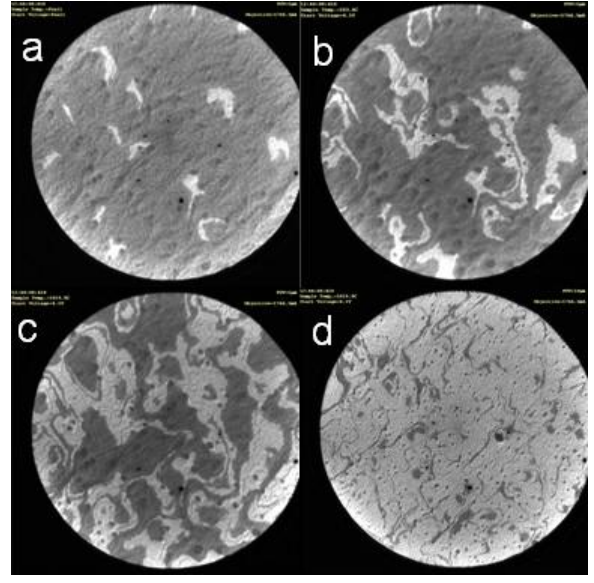


Figure 14: Phase transition of surface from (4×4) to $(\sqrt{3} \times \sqrt{3}) R30^\circ$. The lighter area is $\sqrt{3}$ and the darker region is (4×4)

Figure 14 shows the transition of the surface from (4×4) to $(\sqrt{3} \times \sqrt{3}) R30^\circ$. The phase transition is first order. Once the phase transition was complete, the surface was covered by an entire monolayer of Ag.

Finally the sample was heated to desorb the Ag. However, after the Ag had completely come off, the temperature was lowered and some of the $\sqrt{3}$ phase reappeared. (Figure 15.)

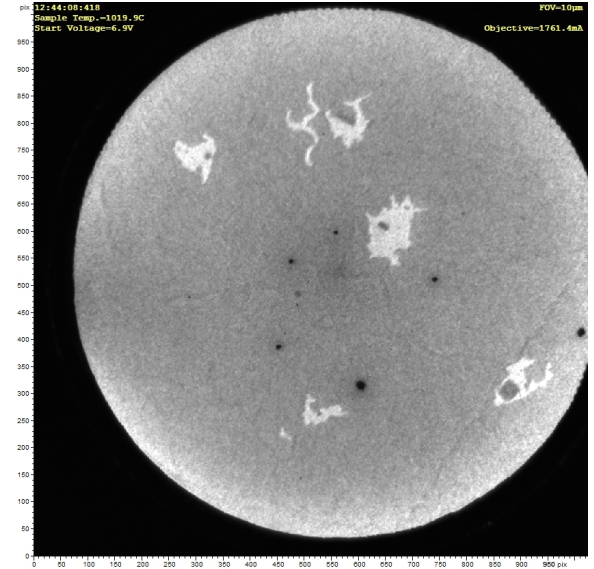


Figure 15: The darker region is $c(2 \times 8)$ germanium, while the lighter region is $\sqrt{3}$ Ag.

This supports the desorption models by Bertucci et al.[10] that predict that some of the Ag adatoms form a 2-dimensional gas phase before evaporating from the surface. Cooling the sample causes these adatoms to recondense on the surface.

3.4 LEEM of Ag on Ge(110)

A sample of Ge(110) was heated to 555°C. The temperature was determined from a calibration which found a relationship between the filament current and the optical pyrometer reading. It was dosed with 9ML of Ag. Figure 16 shows the growth of the Ag islands.

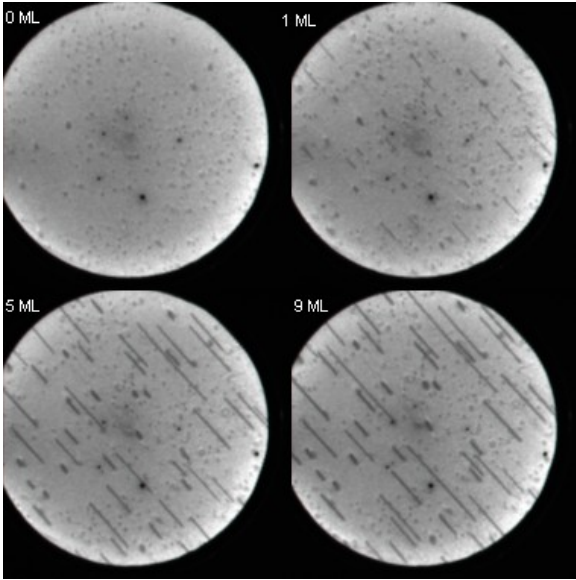


Figure 16: *The islands are getting progressively longer as the silver coverage is increased.*

This growth was observed at several different temperatures. Figure 17 shows how 9ML Ag coverage differs under varying temperatures.

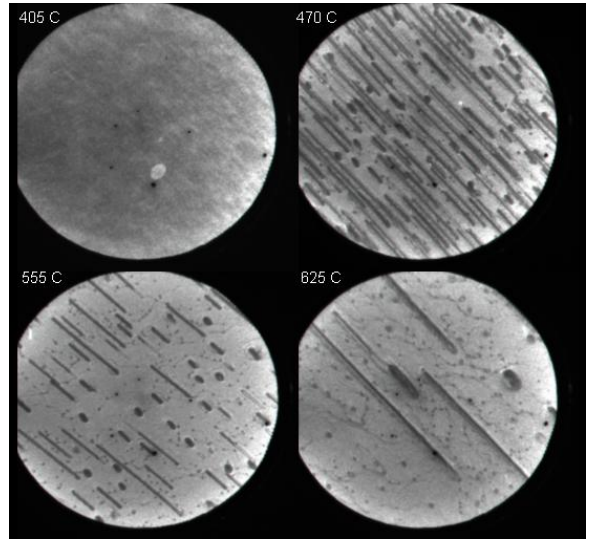


Figure 17: *9ML Ag on Ge(110) at four different temperatures. The bright spot on the 405°C image is a transient defect and not a differing phase.*

The linear islands formed are thin, short, and dense at lower temperatures. As the temperature gets higher, there are fewer islands which are more spread out as well as longer and wider.

After 9ML of growth, the sample was heated in order to desorb the silver. Figure 18 shows the process of silver desorption, for silver which had been adsorbed at 624°C.

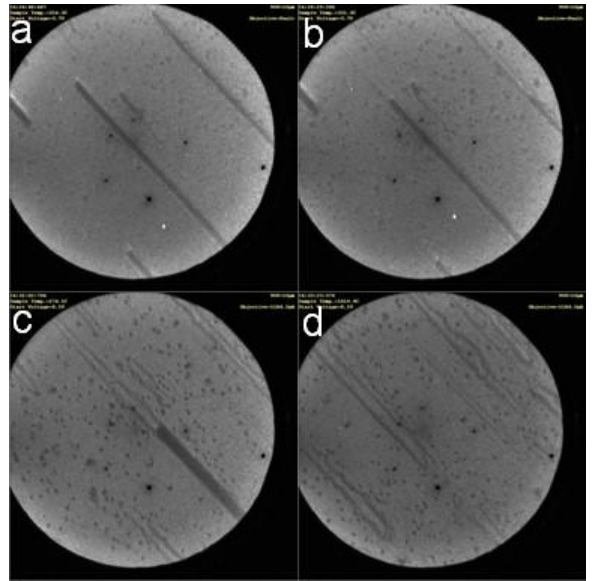


Figure 18: *The desorption began at 717°C and went consistently at 736°C*

As seen in Figure 18, all but the outer edges of the

islands desorbed. The desorption began at the ends of the islands and worked its way to the center.

After the Ge sample had been heated to 406°C and dosing had begun, the surface underwent a phase transition observable by LEEM before the occurrence of any noticeable Ag island formation. (Figure 19) The LEED pattern for this phase is unknown.

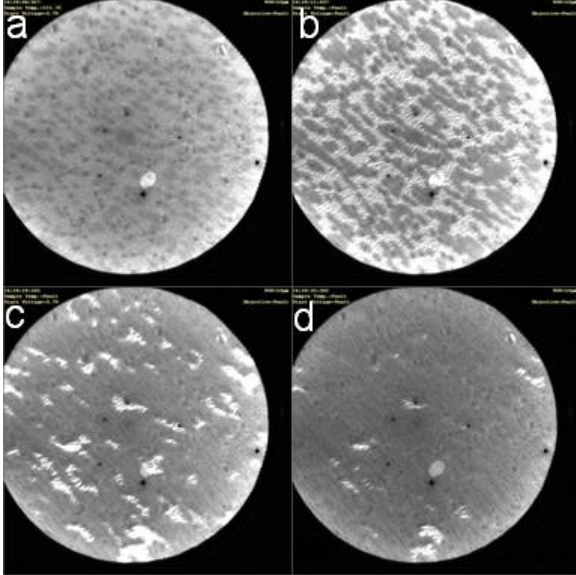


Figure 19: *Light colored regions are original phase while darker colored regions are new phase. The bright spot is a transient defect in image.*

This phase transition only appeared to occur at the low temperature and was first-order. The phase of the surface after the transition is unknown.

4 Conclusions

4.1 STM of Ag on Ge(111)

At 1/2ML of Ag dosed on Ge(111), annealed at 450K for 5 minutes, (3x1) and (4x4) phases of silver coexist along with the c(2x8) phase of germanium. The germanium c(2x8) phase is distorted by competing hexagonal and square (2x2) domains. The (3x1) phase grows along the phase boundary of the (4x4) region. The silver grows in triangular domains.

4.2 STM of Ir on Ge(111)

At 1/2ML of Ir dosed on Ge(111), annealed at 750K for 5 minutes, the germanium surface is distorted such that the c(2x8) phase is competing with a square lattice phase. The Ir spreads evenly over the surface,

but then forms islands over the smooth layers, thus exhibiting the Stranski-Krastanov growth mode.

4.3 LEEM of Ag on Ge(111)

As the dosage of Ag on Ge(111) increases from 0ML to 1ML, the surface undergoes two phase transitions: first from c(2x8) to (4x4), then from (4x4) to $(\sqrt{3} \times \sqrt{3})R30^\circ$. Both transitions are first order. When the silver desorbs, some of the adatoms form a 2-dimensional gas phase above the surface.

4.4 LEEM of Ag on Ge(110)

When dosed on Ge(110), the silver forms linear islands. These islands grow wider, longer, and further apart at higher dosing temperatures. The islands desorb from the inside first. At low dosing temperature, a phase transition occurs on the germanium substrate.

5 Future Work

STM experiments of Ir on Ge(111) will continue in an attempt to achieve atomic resolution of the iridium. Since the LEED patterns suggest a sqrt 3 phase for the iridium, more detailed agreement with the STM data is desired. Additional LEEM measurements of Ag on Ge(110) at lower temperature will be performed, and LEED will be used to try to identify the phase.

6 Acknowledgements

6.1 Collaborators

I would like to thank Cory Mullet and Marshall Van Zijl for showing me how to operate the LEEM and STM equipment, as well risking their experiments by allowing me to operate the equipment; Dr. Shirley Chiang for the direction and explanations she gave me throughout the program; Dr. Rena Zieve for organizing and heading up the UCD Physics REU program.

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