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Kinetics of Solid Phase Crystallization of a-Ge Thin Films

Abstract

A method was developed to investigate the solid-phase crystallization (SPC) reaction undergone by germanium thin films. Amorphous films were grown by the radio-frequency (RF) magnetron sputtering and then annealed for a maximum of 6 hours at two temperatures: 446°C and 460°C. Crystallinity was measured by resistivity measurements, as well as crystal peak height and area taken from X-ray diffractometer (XRD) data. Initial data shows qualitative agreement with a nucleation-growth model for the observed kinetic process. However, observed peak narrowing phenomena suggests a comprehensive model of XRD measurements of polycrystalline thin films is needed for a rigorous interpretation of the results.

Keywords

thin film, Ge, kinetics, solid state, sputtering

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I. INTRODUCTION

Germanium (Ge) thin films have been used for a variety of applications, including recently for the construction of multi-junction photovoltaic cells. The relatively low cost of thin films compared to their macroscopic counterparts has spurred researchers [1] to strive to improve the crystalline quality of Ge thin films grown by *in situ* deposition and *ex situ* solid-phase crystallization (SPC). While the kinetics of the SPC process have been studied extensively for Silicon (Si) films, less is known about the specifics of the process for Ge films. Thus in this work we perform a kinetic characterization of the SPC process for Ge thin films grown by radio-frequency (RF) magnetron sputtering. RF sputtering has been used [3] to grow films in both amorphous or crystalline states, depending on the substrate temperature. Ge films grown by this technique with substrate temperatures below about 254° C are amorphous, and make good candidates for a SPC kinetics characterization [5].

We adopt a method similar to that used by Hong and Ro [2] to study the kinetics of Si thin films, but focus on the 446° C - 460° C temperature regime to observe the expected sigmoid curve of crystalline fraction versus time. A classical model is often used to explain this process for Si, consisting of an amorphous incubation period, followed by an initial nucleation period, which then leads to (relatively) rapid crystal grain growth until crystal saturation [4]. If the SPC process for Ge consists of this same localized nucleation and growth, a similar sigmoid curve should be observed.

II. METHODS

The following procedure was carried out for each individual thin film in our experiment.

A. Film Growth and Preparation

Amorphous films were grown in a vacuum chamber by RF magnetron sputtering. The chamber was evacuated to 5.0×10^{-8} torr, and then a 1×1 inch glass substrate was inserted into the vacuum chamber via a loadlock system. The substrate was removed from its sealed packaging and immediately placed in the chamber to avoid contamination. The chamber was then filled with 8.00 millitorr of Argon gas, and the substrate was heated to a temperature of 150°C, and an RF discharge was initialized. After a 10 minute pre-sputter to remove any impurities on the surface of the 99.999% germanium wafer target, the sputtering shutter was removed from the substrate for deposition to begin. Films were deposited for 30 minutes, then allowed to cool to room temperature before *ex situ* crystallization. These parameters yielded an average film thickness of 3300 Å, as estimated from a previously measured deposition rate.

In order to maximize the number of usable films, each 1×1 inch film was then cut into four $\frac{1}{4}\times\frac{1}{4}$ inch films. This allowed a greater data yield over the short lifespan of the experiment. The films were cut using a diamond wet saw. Next each sample was rinsed with water, then distilled water and methanol, and was finally dried using a cool-air dryer and vacuum. Measurements of film resistivity and XRD crystalline peak height of test films before and after the cutting procedure were found to agree to within uncertainties, and thus this technique was deemed worthwhile to maximize data yield.

B. Crystallinity Proxies

Past research [5] on germanium thin films has shown that those grown by magnetron sputtering below a substrate temperature of 254°C were amorphous. To comfirm this in our samples, each was tested before annealing to ensure a uniform amorphous starting point across samples. Two diagnostic tests were performed as a baseline check of amorphous film quality: a resistivity measurement and X-Ray Diffractometer scan. Resistivity measurements were performed using a four-point probe. This test can be used as a rough estimate of crystallinity, due to the rapid orders-of-magnitude drop off in resistivity during crystallization [5]. Each film was confirmed to have a starting resistivity of approximately 300Ω·cm, consistent with amorphous films. The XRD pre-anneal scan was purely qualitative, to make sure that no crystalline peaks were detected before annealing. A comparison between the amorphous and crystalline signatures of the films we used can be seen in FIG. 1. The difference between an amorphous and a crystalline film suggests that the XRD scan could be used to measure the extent of crystallization.

C. Annealing process

Films were annealed in a tube furnace for various times ranging from 30 minutes to 6 hours, at two fixed temperatures, 446°C and 460°C. These temperatures were chosen to allow the crystallization processto be tracked from fully amorphous to fully crystalline. A constant flow of 5 SCF/h of N_2 gas was flowed through the furnace to prevent oxidation of the samples at high temperatures. The tube furnace was heated to a desired set point temperature, and then at $t = 0$ the sample was introduced into the temperature-controlled zone of the furnace and allowed to heat up. Temperature was monitored by an *in situ* thermocouple wire attached to the substrate holder. The substrate holder was found to take approximately 12 minutes to equilibrate to within 1% of the set point temperature. At the end of the anneal duration, the sample was immediately removed from the heated zone of the furnace and allowed to cool, with N_2 still flowing to avoid oxidization.

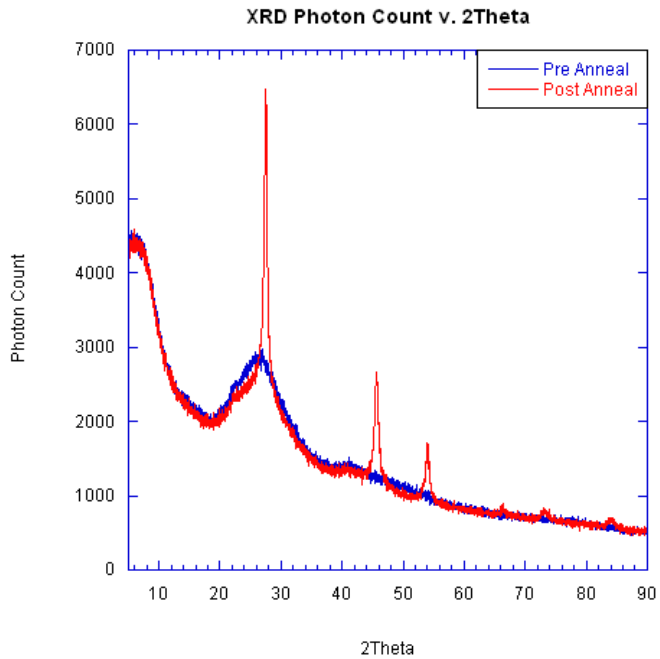

FIG. 1. X-Ray Diffractometer photon counts versus angle 2-Theta for a film pre- and post-anneal.

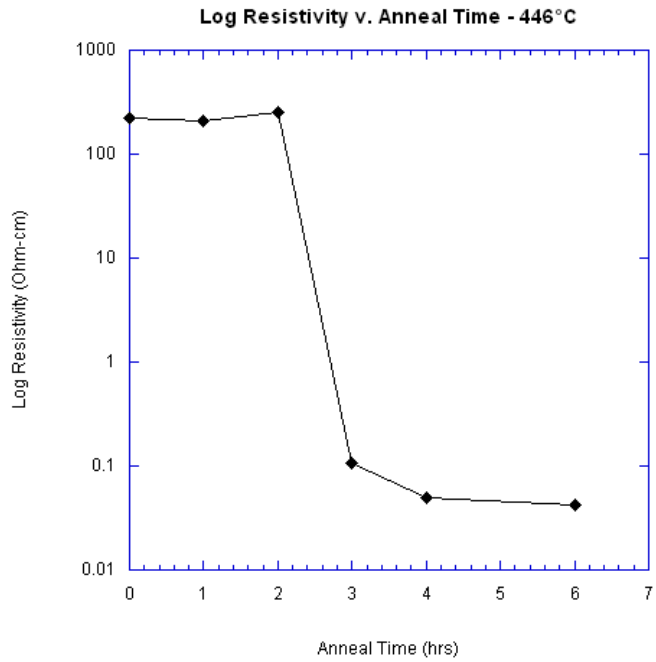

FIG. 2. Log of resistivity (in Ohm-cm) versus anneal time in hours, for a constant T=446°C.

D. Post-Anneal Diagnostics

After annealing, two quantitative measurements were made on each sample. The resistivity of each sample was measured and plotted as a function of time in FIG. 2 and FIG. 3. Then each sample was analyzed using XRD. High-sensitivity was achieved using a 10-scan average. Two metrics, peak height and peak area, for the $(1,1,1)$, $(3,1,1)$ and $(2,2,0)$ crystal orientations were extracted from these XRD scans, and plotted as a function of time in FIG. 4-7. The data were measured from a standardized background determined by the *X'Pert HighScore Plus* data analysis software.

III. RESULTS & DISCUSSION

A. Resistivity

A logarithmic plot of resistivity versus anneal time for films annealed at 446°C shown in FIG. 2 shows a relatively constant resistivity for $t < 2$ hrs, followed by a rapid drop by a factor of 1000 observed at hour 3. There is insignificant change between hours 4 and 6. Based on this data alone, it would seem that the films began crystallizing rapidly shortly after the two hour mark, and reached a saturation point by hour 4, where it remained until hour 6.

The 460°C data set behaves quite similarly, though in this case we were able to get a data point in the middle of the rapid drop, from a measurement taken at 53 minutes anneal time. The films remained amorphous up until 43 minutes, and then fully crystalline after 75 minutes. This graph has the same inverted sigmoid shape as the 446°C sample, but compressed in time. This is consistent with the theory that temperature should have a positive correlation with SPC reaction rate, and thus a negative correlation with crystallization time.

B. Peak Height

Using XRD data, there was no evidence of crystallization for the 446°C films until after the 1 hour mark. This can be seen in FIG. 4 as none of the crystal orientations had shifted from baseline. A rapid period of crystallization occurred between hours 2 and 4, followed by saturation. We note that the $(2,2,0)$ peak actually *decreased* in height between hours 4 and 6. This decrease could be due to a change in preferred orientation of the crystallites at $t > 4$ hrs, or even just uncertainting in accurately determining the peak heights. The average peak height does appear to saturate at 4 hours within measurement uncertainty, consistent with the resistivity data.

For the 460°C sample shown in FIG. 5, no peaks appeared until after 43 minutes. The 77 minutes saw a rapid increase in peak heights, saturating after 2 hours. Note that for this temperature, none of the crystal orientations showed a decrease in peak magnitude. The average continued to slightly rise into the third hour. It appears that crystallization is not complete after the 2 hour point, but continues to proceed at a very slow rate.

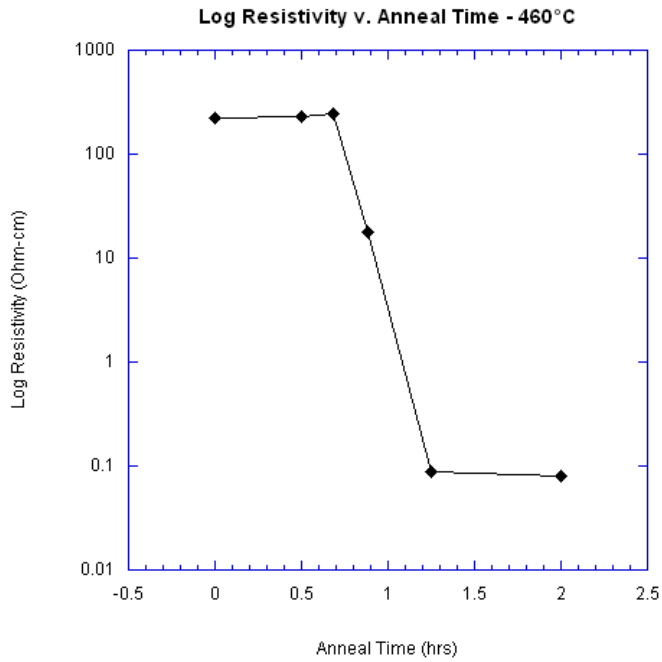

FIG. 3. Log of resistivity (in Ohm-cm) versus anneal time in hours, for a constant T=460°C.

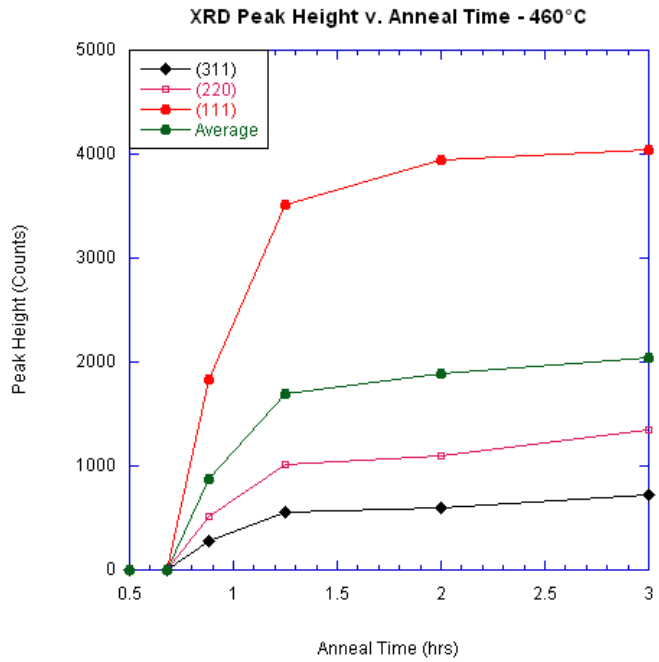

FIG. 5. XRD peak height versus anneal time in hours, for a constant T=460°C.

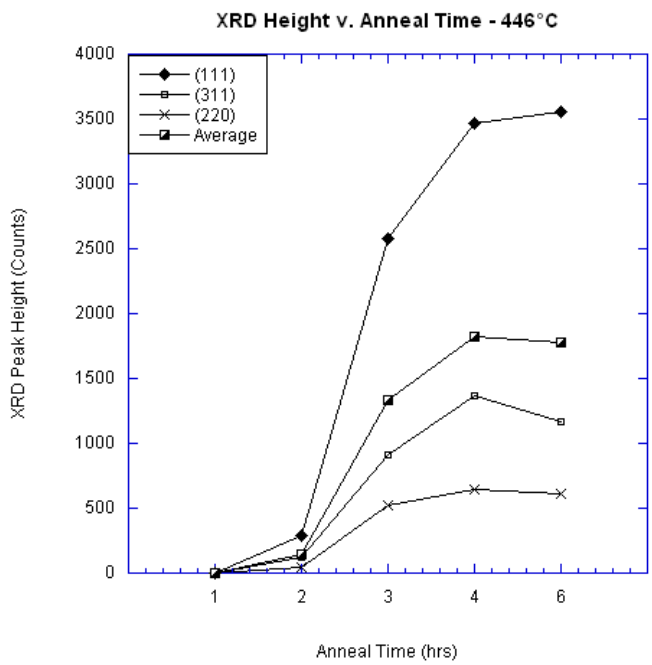

FIG. 4. XRD peak height versus anneal time in hours, for a constant T=446°C.

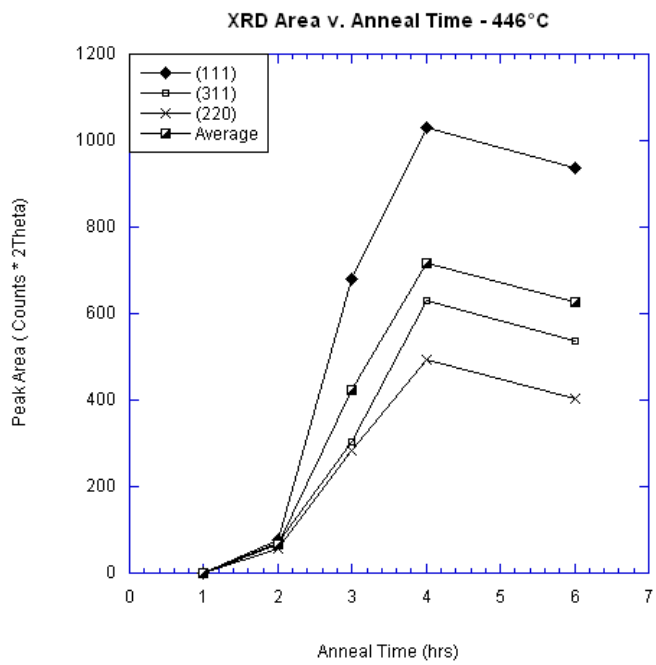

FIG. 6. XRD peak area versus anneal time in hours, for a constant T=446°C.

C. Peak Area

In addition to the XRD peak heights, another measure of crystalline magnitude available from the XRD data is peak area. FIG. 6 shows the same induction period of about 1 hour similar to that observed from the peak height data, and then a very similar rapid increase. In this case the area under *all* peaks decreased between hours 4 and 6.

Peak area data for the 460°C series is even more striking. While the first part of the curve exhibits the expected behavior, the final data point dropped for each

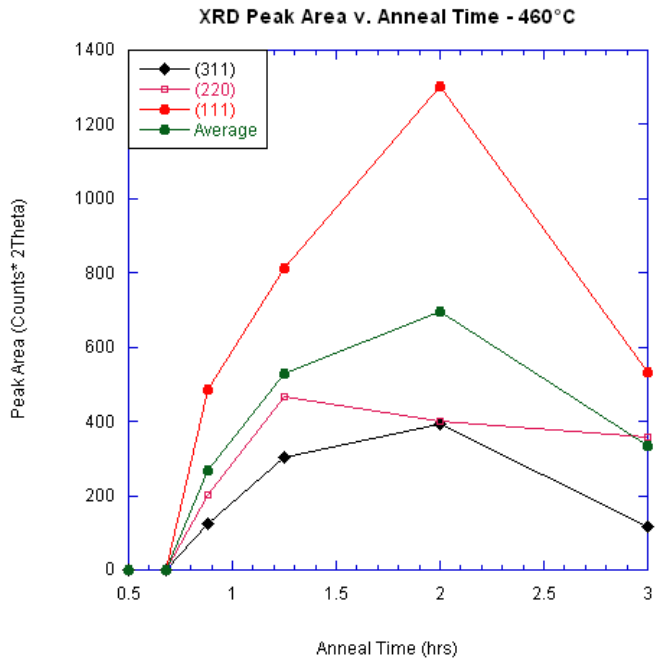

FIG. 7. XRD peak area versus anneal time in hours, for a constant T=460°C.

crystal orientation, even more drastically than in the 446°C series. Thus, the peak area metric appears to be consistent with neither the peak height results northe resistivity results. Furthermore, it has the non-intuitive results that the crystallinity of the films are *decreasing* with anneal time.

D. Discussion

Both resistivity and peak height seemed to capture the qualitative essence of what we would expect from a SPC process that proceeds by the process of nucleation, grain growth, and then complete crystallization. That is, we see a sigmoid curve showing an induction period, a section of rapid change, and then saturation. However, more data is needed to make a quantitative argument.

Initially it seems intuitive that peak area would be a good quantitative measure of crystalline fraction. However, such an interpretation of the peak area is complicated by the dependence of peak width on other factors. For example, it is well known that the peak width has an inverse dependence on both crystallite size and film stress (and in fact can be used to estimate these parameters). These factors suggest a possible explanation for the saturation of peak height with anneal time accompanied by a decrease in the peak area. Peak height could be strongly correlated with crystallite fraction, which is relatively independent of crystallite size, whereas for longer anneal times the crystallite size increases, thereby decreasing the peak width and hence the peak area. In effect, as smaller crystallites merge during longer anneal times, the net crystalline fraction does not change appreciably (giving the saturation in peak height observed) but the larger crystallites result in a narrower peak width. Lower film stress resulting from longer anneal times could also produce similar effects. Independent measurements of crystalline size (using transmission electron microscope for example) and film stress could provide corroboration of this hypothesis. Larger crystallite sizes should also influence the electrical transport properties. There does seem to be a slight decrease in resistivity for the longer anneal times (see FIG. 2,3), which could be due to a slight increase in mobility due to the larger crystallite size (or decreasing stress). This interpretation is complicated by possible changes in carrier concentration due to defect doping. Hall effect measurements could be used to more fully elucidate these effects.

Although this proposal gives a consistent account of the resistivity, peak height, and peak area results, there are possible complications. For example, one might expect that at least with the growing crystallite size hypothesis that the total area under the peak should still be conserved, resulting in an increase of peak height with narrowing width. A comprehensive model of XRD measurements for polycrystalline thin films would be needed to rigorously interpret these results. At this time though, no such model exists. However, further insight could be gained using complementary methods of crystallinity determination such as Raman scattering and spectroscopic ellipsometry.

Raman spectroscopy has been used to measure the crystalline fraction of silicon [2], but it turns out that germanium presents it's own unique set of problems for raman spectroscopy as well. The raman shift measured is less pronounced that that of silicon [5], and thus would likely have a lower resolution, making it non-ideal for measuring small changes in crystallinity, which are needed for kinetic modeling.

Spectroscopic ellipsometry is often used to infer crystallinity, but that technique requires a sophisticated understanding of the optical properties of the material being studied. In addition, the large number of adjustable parameters needed result in difficulties with uniqueness of interpretation.

IV. SUMMARY & CONCLUSIONS

In summary, a method was developed to investigate the kinetics of the solid state reaction that occurs as germanium thin films are heated to their crystallization point. Films were grown by RF magnetron sputtering, verified to be amorphous, and then annealed at 446°C and 460°C for various anneal times. Three measurements of crystallinity were taken: Resistivity, XRD peak height, and XRD peak area. All three measurements showed a sigmoid shape, providing support for a nucleation-growth model of germanium crystallization. However, the XRD peak area measurement is complicated by peak narrowing

processes. Stronger theoretical grounding is needed to fully interpret the XRD spectra as metrics of crystalline fraction. Other methods of measuring crystallinity such as Raman spectroscopy and spectroscopic ellipsometry may also be needed to complement the XRD measurements.

V. ACKNOWLEDGMENTS

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