A Comparison of Silicon Germanium Oxide Growth and the Deal-Grove Model

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Silicon germanium is an area of interest for researchers in silicon photonics, as the addition of germanium can alter the bandgap of silicon, leading to the possibility of light detection or production in silicon. The oxidation of silicon is well described by the Deal-Grove model, but the oxidation of SiGe is more difficult to predict due to a variety of factors that affect oxide growth. This study attempts to give a comparison between SiGe oxide growth and the Deal-Grove model for better understanding of which rate is dominating at different times and oxide thicknesses. The data collected in this study was collected for the purpose of studying the germanium profile in the SiGe after oxidation, but for this study the oxide thicknesses will be investigated. Due to large uncertainties and an insufficient amount of data points to draw definite conclusions, the main purpose of this study will be to act as a precursor to a more in depth study, and the areas which need improvements will be looked at and improved for the next study. The results found in this study support the expectation that the SiGe growth is more rapid than pure silicon, and finds that the growth rate levels off as the oxide becomes thicker in a possibly parabolic manner, similar to the Deal-Grove model.

I. INTRODUCTION

While silicon is an evidently major component in silicon photonics, it lacks two essential abilities: light detection and emission. The use of silicon germanium in silicon photonics is an area of interest due to its ability to change silicon's band gap to be direct, which can enable photon detection and emission. While a silicon-based light detector and emitter have cost benefits, the manufacturing processes for SiGe have different considerations than those for pure silicon, in particular the oxide growth process, which must be investigated before large-scale manufacturing can be a possibility. The growth of thermal oxide on pure silicon is a well understood phenomenon, with the Deal-Grove model being able to accurately describe it for flat surfaces [1], but this process is affected by the addition of germanium. Knowing how the oxidation of SiGe occurs as well as the diffusion of germanium into the silicon has the potential to predict the germanium profile in the alloy, which is beneficial to the manufacturing of SiGe for silicon photonics when a certain composition of SiGe is desired. The purpose of this study is to compare the Deal-Grove model predictions of pure silicon to the oxide growth of SiGe. The results will be used to design a more in-depth study that looks at multiple concentrations of implanted germanium and improve any areas of the study that need attention, in order to achieve reliable and useful results in the next study.

The Deal-Grove model uses two competing rates to model the oxide growth of silicon. This model assumes that the oxidation reaction occurs at the silicon oxide-silicon interface. The two rates are the diffusion rate of oxidants through the oxide and the reaction rate at the interface.

These rates must be equal since they occur in series, the slowest one determines the total oxidation rate. The rate that is the slowest depends on the thickness of the oxide and the temperature. Qualitatively, it is easy to understand that with thinner oxides the oxidant can reach the interface very quickly, supplying the oxidation reaction with ample oxidant, and so the reaction rate is the slowest rate in this case. For thicker oxides, it takes longer for the oxidants to diffuse through and this rate becomes the slowest of the two. The Deal-Grove model is also called the linear parabolic model, due to the shape the oxide thickness-time function takes in the two regions-the initial, thin oxide region where the reaction rate determines the growth rate is linear, while the later, thick oxide region where the diffusion rate dominates, has a parabolic relationship. Note that this parabolic relationship is for time as a function of thickness, meaning that for thickness as a function of time the relationship is similar to that of a square-root. [2]

When germanium is introduced to the silicon oxidation process, a variety of factors must be considered. Ultimately, the introduction of germanium has been shown to enhance oxidation rate. It is hypothesized that the diffusion rate should be the same in both Si and SiGe, assuming no germanium dioxide is formed. This is a valid assumption to make considering GeO2 has been seen formed at low temperatures [3], high pressures [4], or high germanium concentration in the alloy [5], none of which are featured in this experiment. It is the reaction rate that does change in Si and SiGe. In only Si, the oxidation reaction comprises of two steps: the breaking of the Si-Si bond, and the formation of SiO2. In silicon that has been implanted with germanium, there are several factors that are different from non-implanted silicon. One factor is that the Si-Ge bond is weaker than the Si-Si

bond, and so takes less time to be broken. Another factor is that GeO is formed faster than SiO2, but much less stable; the germanium in the GeO can then be easily replaced by a Si atom and quickly form SiO2. This process is faster than the direct synthesis of SiO2 from Si and O2. A third factor is point defects, which enhance the reaction rates of both Si and Ge, particularly in wet oxidation, but this is not investigated in this experimented [6].

This study aims to observe the change of rate determining step from the reaction rate to the diffusion rate, specifically in comparison to the Deal-Grove model for a pure silicon sample under the same conditions.

A. Experimental Setup

For this experiment, 42 samples of lightly doped n-type (100) silicon implanted with 1e17 atoms/cm^3 germanium at 20keV were used. An initial native oxide thickness of 1nm was assumed for modelling purposes. 18 samples were used for dry oxidation and 24 samples were used for wet oxidation.

For dry oxidation, six temperatures in the range of 900°C to 1050°C were used, each for 5, 15, and 30 minutes. For wet oxidation, eight temperatures in the range 820°C to 1100°C were used, each for 5, 15, and 30 minutes. A Rapid Thermal Annealer (RTA) was used for dry oxidation, where the chamber was pumped with oxygen gas for the desired amount of time when it had reached the temperature, and pumped with nitrogen gas when heating and cooling the chamber for a precise oxidation time period.

A furnace with oxygen flowed through boiling water was used for wet oxidation. The time began as soon as the sample was slid into the middle of the furnace (where the thermocouple measured the temperature) and the sample was removed from the furnace as the time was up.

To measure the oxide thickness, an ellipsometer was used. This device uses the known refractive index of a material and measures the polarization change over different angles using multiple wavelengths of light to find the thicknesses of thin films. For the Deal-Grove model, type (100) silicon was used in the simulations, from the University of Illinois at Urbana-Champaign website.

II. RESULTS

In this section the results of the oxidations will be presented. The uncertainty in many important measurement tools, such as the temperature of the furnace and the ellipsometer thickness measurements, are unknown and therefore no error margins are included in the figures. This will be addressed for the follow-up experiment; for more information, please see the Conclusions section. The accuracy of each data-point is not the main focus of
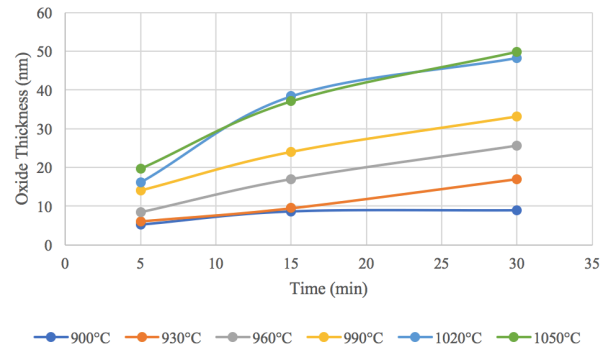

FIG. 1. Oxide growth due to dry oxidation over time for multiple temperatures. The times used were 5, 15, and 30 minutes, and the temperatures were 900°C, 930°C, 960°C, 990°C, 1020°C, and 1050°C.

this experiment– rather the trends that can be seen are what is being looked at, as to have some clarity in the predictions for the next iteration of this experiment.

A. Dry Oxidation

Figure 1 shows the complete data set for the samples that underwent dry oxidation. At high temperatures, the parabolic trend can be noticed, while the low temperatures seem to be to follow a linear trend. Figure 2 shows the oxide thickness predicted by the Deal-Grove model divided by the thickness of the silicon oxide grown on the silicon germanium. This method allows for the relative comparison of the pure silicon oxide growth and the silicon germanium oxide growth.

B. Wet Oxidation

Figure 3 shows the complete data set for the samples that underwent dry oxidation. Like with dry oxidation, the higher temperatures show a more parabolic trend, while lower temperatures are more linear, though still more parabolic than the dry oxidation. This is expected, since wet oxidation results in faster oxide growth in pure silicon compared to dry oxidation. Figure 4, like Figure 2, shows the oxide thickness predicted by the Deal-Grove model divided by the thickness of the silicon oxide grown on the silicon germanium.
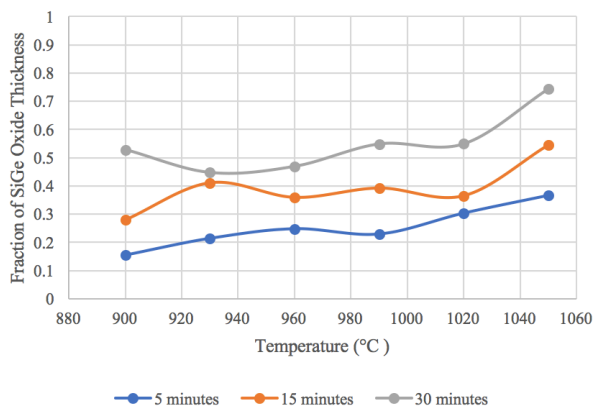
FIG. 2. Relative difference of SiGe oxide thickness compared to Deal-Grove model Si oxide thickness, taken by dividing the latter by the former.
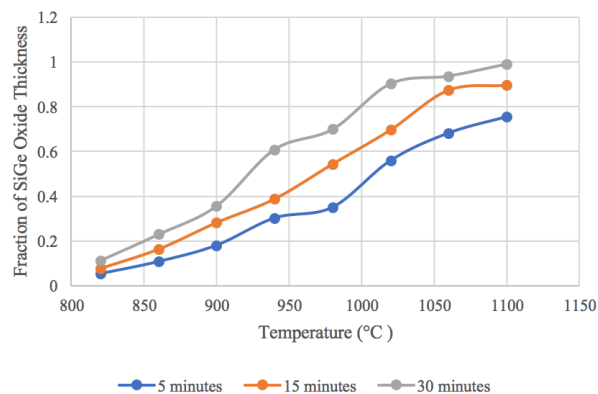

FIG. 4. Relative difference of SiGe oxide thickness compared to Deal-Grove model Si oxide thickness, taken by dividing the latter by the former. These results are from wet oxidation.
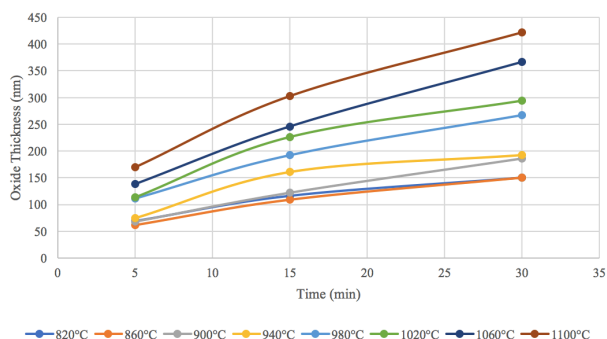

FIG. 3. Oxide growth due to wet oxidation over time for multiple temperatures. The times used were 5, 15, and 30 minutes, and the temperatures were 820°C, 860°C, 900°C, 940°C, 980°C, 1020°C, 1060°C, and 1100°C.

III. CONCLUSION

Like the Deal-Grove model, the higher temperatures increase the oxide growth rate, and so the samples at higher temperatures exhibit a more parabolic shape than the lower temperatures; this is due to the oxide growing thicker more quickly and therefore the oxide diffusion rate becoming the slower rate (see figures 1 and 3). Due to there being only three data points for each temperature, however, it is not possible to see the point where the rates change, nor is it possible to determine whether the reaction rate for smaller oxide thicknesses is linear like the Deal-Grove model.

In figures 2 and 4, it can be seen that the relative difference between the SiGe oxide thickness and the Deal-Grove-predicted thicknesses increase with time as well as with temperature. The wet oxidation at the highest time (30 minutes) and temperature (1100°C) produced a thickness that was extremely close to that predicted by the Deal-Grove model. This is interesting because according to the hypothesis, the rate determining factor with thicker oxides should be the diffusion of oxidants through the oxide, which should be the same for SiGe and the Deal-Grove model after a certain thickness. Since this rate gives a parabolic relationship to thickness and time, it is surprising for the two thicknesses to converge after only 30 minutes, and to have gotten to around 75% after only 5 minutes. This suggest that there is very rapid growth in the first five minutes and then the rate seems to decrease significantlyhowever, these results may not be accurate, as will be discussed in the next paragraph. Unfortunately, again, there is not enough data to see how exactly the rates change with time.

Another interesting observation is that the relative thickness after five minutes is consistently lower than that at 15 minutes, which likewise is consistently lower than the relative thickness at 30 minutes. This suggests that though at less than five minutes the pure silicon growth rate is lower than that of the SiGe, the pure silicon growth rate begins to increase more quickly than that of the SiGe. The conclusion from this observation is that the SiGe oxide growth rate levels off significantly, likely at less than five minutes, in addition to the convergence of the oxide thicknesses at higher temperatures. Further experimentation could be done to determine if at even longer times, the relative thickness for pure silicon and SiGe would converge at 100%.

Alas, the results for the wet oxidation have a further problem with them: the wet oxidation furnace was found, after the fact, to be as much as 30°C below the set tem-

perature, which could account for why the SiGe and Deal-Grove thicknesses converged so quickly. The RTA for dry oxidations, however, had very recently been calibrates, and so the interpretations of the dry oxidation results can be relied on to a greater degree. The uncertainties in the ellipsometry data also must be investigated further, because of the fluctuations in figure 2 at low oxide thicknesses are likely due to a systematic error in the ellipsometry measurements that translated into large relative error in the division to find the relative difference.

Two other sources of error are the temperature profile in the wet oxidation furnace, which drops of rapidly away from the thermocouple in the center, and the assumption of the 1nm native oxide on the samples. Any uncertainty in the temperature of the wet oxidation furnace can be resolved easily by including a non-implanted silicon sample in the oxidation, and then use the Deal-Grove model to find the actual temperature the samples were exposed to. The native oxide might not be 1nm, which is a fair assumption for silicon but could be different for silicon germanium. This can be investigated through initial ellipsometry data being taken. The uncertainty in the ellipsometry data can also be addressed by comparing the measurements with a more accurate method of measuring oxide thicknesses: Rutherford backscattering (RBS).

With the considerations found in this study, a follow-up study that addresses the areas of weakness found in this one can be designed. More data points at lower times are needed, along with non-implanted silicon samples to accompany the SiGe samples in the wet oxidation furnace. The method of measurement should be looked into to find the degree of uncertainty present, and a secondary method of measurement, such as RBS, should be utilized to verify the results. With these alterations, an accurate comparison of SiGe oxide growth and the Deal-Grove model can be made.

Notes and References

[1] B. E. Deal and A. S. Grove. General Relationship for the Thermal Oxidation of Silicon. *J. Appl. Phys.*, 36:3770–3778, 1965.

[2] J. D. Plummer, M. D. Deal, and Griffin P. B. *Silicon VLSI Technology.* Prentice Hall, 2012.

[3] W. S. Liu, E. W. Lee, M-A. Nicolet, V. Arbet-Engels, K. L. Wang, N. M. Abuhadba, and C. R. Aita. Wet Oxidation for the GeSi at 700C. *J. Appl. Phys.*, 71:4015, 1992.

[4] M. A. Rabie, Y. M. Haddara, and J. Carette. A Kinetic Model for the oxidation of Silicon Germanium Alloys. *J. Appl. Phys.*, 98, 2005.

[5] D. C. Paine, C. Caragianis, and A. F. Schwartzman. Oxidation of $Si_{1-x}Ge_x$ Alloys at Atmospheric and Elevated Pressure. *J. Appl. Phys.*, 70:5076, 1991.

[6] J. P. Zhang, P. L. F. Hemment, S. M. Newstead, A. R. Powell, T. E. Whall, and E. H. C. Parker. A Comparison of the Behaviour of $Si_{0.5}Ge_{0.5}$ Alloy During Dry and Wet Oxidation. *Thin Solid Films*, 222:141–144, 1992.