

Novel Experimentally Calibrated Multiphase TCAD Model for Cobalt Germanide Growth

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Abstract—We propose the first multiphase TCAD cobalt germanide growth model that can predict the resulting phase based on germanidation time, temperature, and ambient. The model has been calibrated to experimental results reported in the literature as well as our own data. This model can help in the design of cobalt germanide contacts with low resistance.

Keywords—silicidation, germanidation, cobalt silicide, cobalt germanide, kinetic model

I. INTRODUCTION

A major change has been seen in the industry in the last two decades with the incorporation of high percentages of Ge in MOSFET devices to benefit from the stress engineering in improving the mobility of carriers in those devices. Silicon germanium and pure germanium metal contacts are formed using both silicides and germanides. The industry has a mature understanding of silicides and they have been used for many decades now.^[1] Less attention has been given to germanides.^[2] Careful selection of contact materials and control of the contact formation process are needed for an efficient contact to the CMOS devices and to minimize the contact resistance. The reduction in the contact resistance is necessary since it contributes directly to the RC circuit delays associated with a signal propagating through the device. RC time delays have become an obstacle in obtaining faster integrated circuits in recent years.

The need for high quality contacts in Ge-based devices is the primary motivation for the study of cobalt germanidation. Cobalt is a good candidate for the contact material in Ge-based devices given its compatibility with silicon process, stability, and low resistivity.^[3,4] The contact resistance contribution from metal resistivity depends on the germanide phase. Resistivities of CoGe and CoGe₂ at room temperature have been reported to be 65.7 and 150 $\mu\Omega\cdot\text{cm}$, respectively.^[5] This wide resistivity range emphasizes the importance of careful cobalt germanide contact design.

The temperature at which each of these phases forms also varies. It is important to understand the phase formation sequence in order to design a high quality, low resistivity cobalt germanide contact that forms at a temperature compatible with the semiconductor process. Cobalt germanidation has been the subject of a number of studies.^[5-12] Different phases have been reported to form during cobalt germanidation including Co₅Ge₃, CoGe, CoGe₂, and Co₅Ge₇. Once the initial phase forms, the sequence of phases to appear

for longer reaction times will be determined by the Co-Ge balance. Under Ge-rich conditions we will move to the right on the phase diagram, whereas Co-rich conditions will drive the reaction to the left on the phase diagram.

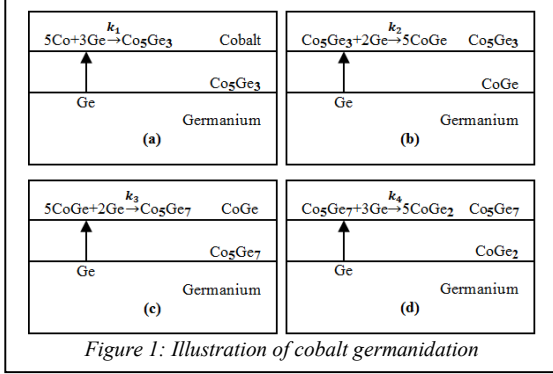
Technology Computer Aided Design (TCAD) models for silicidation are being used in the industry to predict the accurate shape of the silicide, the effect of silicidation on the dopant profiles, and the stress in silicon resulting from silicidation.^[1] These predictive models help in designing devices as well as understanding unwanted behavior resulting from the process steps. TCAD saves the industry time and money that can otherwise be spent on expensive and time consuming experiments. Multiphase silicide models have gained importance in recent years with the use of nickel silicides.^[13] Nickel silicides have multiple phases with different resistivities. It is important for the process designer to design the process in such a way to obtain the specific silicide with the target resistivity. The process can be accurately designed using TCAD simulations.

Cobalt germanidation has multiple phase outcomes similar to nickel silicidation. The process is also very similar since the cobalt is deposited on germanium as nickel is deposited on silicon. The wafer is, then, annealed to obtain the desired silicide or germanide. There are no reports in the literature on the progress of the cobalt germanide thickness with anneal temperature and time. However, there are many^[5-12] reports for the dependence of the resulting phase on time, temperature, and ambient of the experiment. These reports are sufficient to calibrate the model parameters to accurately predict the cobalt germanide phase depending on time, temperature, and ambient of the process. In addition, the thickness dependence can also be obtained given the phase transformation with the process conditions. The model is described in the next section and the simulation results are discussed in the third section of this paper.

II. THE MODEL

Co₅Ge₃ is the first phase to form by diffusion of Ge through the forming Co₅Ge₃ layer and the reaction of Ge and Co at the Co₅Ge₃-Co interface to form new Co₅Ge₃ layers.^[4, 14] Cobalt germanidation process is illustrated in figure 1. The EHF model^[15] predictions and experimental results^[3, 4] show that, in the presence of excess Ge, the next phase to form is CoGe which is the phase to the right of Co₅Ge₃ in the phase diagram.^[16] CoGe will not form until either all cobalt is

consumed or the thickness of the Co_5Ge_3 layer causes the germanidation reaction to become diffusion limited. CoGe and Co_5Ge_3 are expected to coexist until cobalt is fully consumed. At that point, Ge will continue to react with Co_5Ge_3 forming CoGe and consuming the remaining Co_5Ge_3 . The next phase to form will be Co_5Ge_7 and finally CoGe_2 . The phases to the left of Co_5Ge_3 in the phase diagram [16] won't form unless Co is in excess of Ge in the system.



During cobalt germanidation, the four reactions shown in figure 1 take place. The reaction rates, k_1 - k_4 , have Arrhenius dependence on temperature similar to the silicon oxidation model.[1] The reverse reactions are thermodynamically unfavorable and have not been reported in the experimental literature previously. Therefore, the reverse reactions are not considered in the TCAD model. The rate of consumption of cobalt is proportional to its reaction rate constant (k_1) with Ge to form Co_5Ge_3 .^[17] k_1 is the reaction constant assuming Co is available at its equilibrium concentration at the reacting interface and, therefore, it needs to be scaled by the actual concentration of cobalt available at the interface: $C_{\text{Co}}/C_{\text{Co}0}$. The rate of generation of Co_5Ge_3 at the Co- Co_5Ge_3 interface is proportional to the concentration of germanium at the interface C_{Ge} . 3 Ge atoms are needed to form one Co_5Ge_3 molecule. Therefore, the rate of generation of Co_5Ge_3 or consumption of Co is proportional to $(1/3)C_{\text{Ge}}$. The rate of consumption of Co is 5 times that of generation of Co_5Ge_3 since it takes 5 Co atoms to form one Co_5Ge_3 molecule:

$$\frac{\partial C_{\text{Co}}}{\partial t} = -\frac{5}{3}k_1 \frac{C_{\text{Co}}}{C_{\text{Co}0}} C_{\text{Ge}} \quad (1)$$

where $C_{\text{Co}0}$ is the solid solubility of cobalt in Co_5Ge_3 . Equation (1) doesn't limit the forming phase at the interface to Co_5Ge_3 ; other phases are possible mathematically despite not physically possible. This has been handled by careful calibration of the model.

Co_5Ge_3 is generated when Co and Ge react and is consumed when Ge reacts with Co_5Ge_3 forming CoGe . 2 Ge atoms are needed in the reaction. Therefore, the rate of consumption of Co_5Ge_3 is proportional to $1/2 C_{\text{Ge}}$. k_2 is the reaction rate assuming the concentration of Co_5Ge_3 is the equilibrium concentration and has to be scaled by the available concentration of Co_5Ge_3 $C_{\text{Co}_5\text{Ge}_3}/C_{\text{Co}_5\text{Ge}_30}$:

$$\frac{\partial C_{\text{Co}_5\text{Ge}_3}}{\partial t} = \frac{1}{3}k_1 \frac{C_{\text{Co}}}{C_{\text{Co}0}} C_{\text{Ge}} - \frac{1}{2}k_2 \frac{C_{\text{Co}_5\text{Ge}_3}}{C_{\text{Co}_5\text{Ge}_30}} C_{\text{Ge}} \quad (2)$$

The constant $C_{\text{Co}_5\text{Ge}_30}$ is the number of Co_5Ge_3 molecules per unit volume in a pure Co_5Ge_3 material.

Equation (2) can be generalized: when a phase is consumed, it contributes to the formation of the next phase. When the right hand side of the above equation yields an overall positive value, it implies Co_5Ge_3 is growing. When it is a negative value, Co_5Ge_3 is being consumed. The generation/consumption of both CoGe and Co_5Ge_7 are very similar in nature to the generation /consumption of Co_5Ge_3 described above. The equations governing their growth /consumption are:

$$\frac{\partial C_{\text{CoGe}}}{\partial t} = \frac{5}{2}k_2 \frac{C_{\text{Co}_5\text{Ge}_3}}{C_{\text{Co}_5\text{Ge}_30}} C_{\text{Ge}} - \frac{5}{2}k_3 \frac{C_{\text{CoGe}}}{C_{\text{CoGe}0}} C_{\text{Ge}} \quad (3)$$

$$\frac{\partial C_{\text{Co}_5\text{Ge}_7}}{\partial t} = \frac{1}{2}k_3 \frac{C_{\text{CoGe}}}{C_{\text{CoGe}0}} C_{\text{Ge}} - \frac{1}{3}k_4 \frac{C_{\text{Co}_5\text{Ge}_7}}{C_{\text{Co}_5\text{Ge}_70}} C_{\text{Ge}} \quad (4)$$

The equation that governs CoGe_2 is slightly different from the equations used for the other phases. The main difference is that CoGe_2 is never consumed, as it is the last phase to form:

$$\frac{\partial C_{\text{CoGe}_2}}{\partial t} = \frac{5}{3}k_4 \frac{C_{\text{Co}_5\text{Ge}_7}}{C_{\text{Co}_5\text{Ge}_70}} C_{\text{Ge}} \quad (5)$$

Since Ge is the diffusing species, the diffusion term of Ge is used to describe the generation rate of Ge. Ge is consumed by reacting with Co or with cobalt germanides forming new phases of cobalt germanides. All 4 phases have to be considered in this case:

$$\frac{\partial C_{\text{Ge}}}{\partial t} = \nabla \cdot (D_{\text{Ge}} \nabla C_{\text{Ge}}) - k_1 \frac{C_{\text{Co}}}{C_{\text{Co}0}} C_{\text{Ge}} - k_2 \frac{C_{\text{Co}_5\text{Ge}_3}}{C_{\text{Co}_5\text{Ge}_30}} C_{\text{Ge}} - k_3 \frac{C_{\text{CoGe}}}{C_{\text{CoGe}0}} C_{\text{Ge}} - k_4 \frac{C_{\text{CoGe}_2}}{C_{\text{CoGe}_20}} C_{\text{Ge}} \quad (6)$$

D_{Ge} is the germanium diffusivity in cobalt germanide and has Arrhenius dependence on temperature.

The flux of Ge at the reacting interface is given by:

$$F_{\text{Ge}} = -D_{\text{Ge}}(C_{\text{Ge}} - C_{\text{Ge}}^*) \quad (7)$$

where C_{Ge}^* is the solid solubility of Ge in cobalt germanide. Germanides react with germanium to form new germanide phases. Germanide flux is given by:

$$F_{\text{Co}_x\text{Ge}_y} = -\frac{m_n r_n}{\Sigma r} F_{\text{Ge}} \quad (8)$$

where r is the multiphase reaction rate for different germanides and m_n is a stoichiometric constant. 3 Ge atoms are needed to form one molecule of Co_5Ge_3 : $m_I=1/3$. r_n and m_n values are presented in table 1.

The consumed volume of cobalt is:

$$\frac{\partial v_{\text{Co Consumed}}}{\partial t} = -5F_{\text{Co}_5\text{Ge}_3} \Omega_{\text{Co}} = -\frac{5\Omega_{\text{Co}} r_1}{3 \Sigma r} F_{\text{Ge}} = -\frac{\beta}{DR} F_{\text{Ge}} \quad (9)$$

where Ω_{Co} is the atomic volume of Co, R is the conversion ratio from consumed material: Co to the growing material: Co_5Ge_3 , D is the density of the growing material: Co_5Ge_3 , and β is a stoichiometric constant. The assumption of the model is that cobalt reacts with germanium forming only Co_5Ge_3 which,

then, reacts with germanium again to form other germanide phases. β and D for various germanides are summarized in table 1.

Table 1: Parameters for different phases

Growing phase	m_n	r_n	β_n	$D_n (cm^{-3})$
Co_5Ge_3	$1/3$	$k_1 \frac{C_{Co}}{C_{Co_0}}$	$5/3$	$1.525083e22$ [18]
$CoGe$	$5/2$	$k_2 \frac{C_{Co_5Ge_3}}{C_{Co_5Ge_3_0}}$	$1/2$	$4.0745208e22$ [19]
Co_5Ge_7	$1/2$	$k_3 \frac{C_{CoGe}}{C_{CoGe_0}}$	$5/2$	$5.9296394e21$ [19]
$CoGe_2$	$5/3$	$k_4 \frac{C_{Co_5Ge_7}}{C_{Co_5Ge_7_0}}$	$1/3$	$2.3082184e22$ [18]

The consumed volumes of the other 3 germanides can be obtained using table 1 in a similar way to equation 9. The total growing volume of the germanide is given by the sum of the growing volumes of the 4 individual germanides:

$$\frac{\partial v_{grow}}{\partial t} = \sum F_{Co_xGe_y} \Omega_{Co_xGe_y} = \frac{\sum \Omega_{Co_xGe_y} r_n m_n}{\sum r} F_{Ge} \quad (10)$$

The consumed volume of Ge is given by:

$$\frac{\partial v_{Ge \text{ Consumed}}}{\partial t} = -F_{Ge} \Omega_{Ge} \quad (11)$$

III. SIMULATION RESULTS

The model parameters were calibrated to correctly predict the resulting phase for different experimental conditions reported in the literature detailed in table 2. Most experiments report the final phase based on measurements. Some experiments didn't report the measured final phase but instead speculated the phase based on other works. The model assumptions and the understanding of the germanidation process have been used in those cases to predict the correct resulting phase. Intermediate phases and germanide thickness progress have not been reported by any researchers. Hsieh et al. [8] reported interfacial reaction at 220°C. Cobalt didn't completely react at that temperature. The researchers weren't able to confirm the resulting phase to be $CoGe$ or Co_5Ge_3 . Based on our results in experiments 1 and 2 [4], we concluded that the resulting phase was Co_5Ge_3 . Cobalt is not completely consumed in experiment 1, since in the longer time experiment 2, Co continues to react with Ge forming new layers of Co_5Ge_3 . Oxidation of cobalt had to be considered for experiments: 3 and 6. After cobalt consumption in experiment 6, Ge reacted with the Co_5Ge_3 resulting in a new phase: $CoGe$ as shown in figure 4. Cobalt is not expected to be completely consumed in experiment 3 as shown in figure 2 since Co_5Ge_3 was detected. Grzela et al. [7] didn't detect the actual forming phase in their experiments. They detected the structural changes in cobalt germanides forming at different temperatures and concluded the forming phases based on other

works. Table 2 shows the expected phases in Grzela et al.'s work based on our model. Figure 3 shows all the results of the experiments 1, 2, 4, and 5. All cobalt is consumed in experiment 8 since the detected phase was Co_5Ge_7 which will only result after Ge reacts with $CoGe$. $CoGe$ forms through the reaction of Ge and Co_5Ge_3 after the consumption of cobalt.

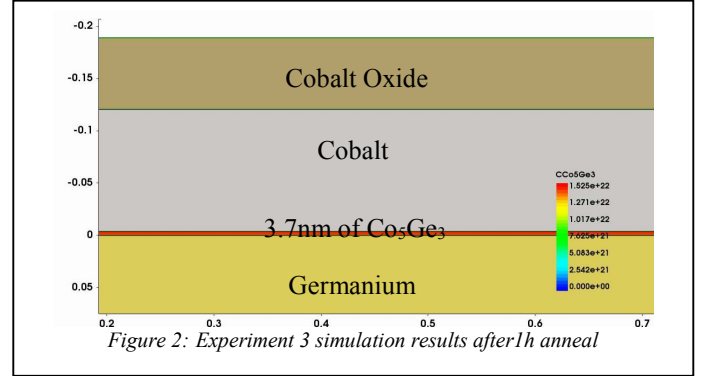


Figure 2: Experiment 3 simulation results after 1h anneal

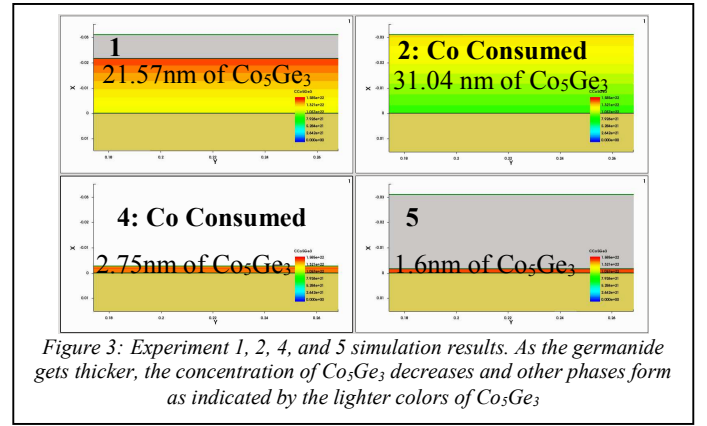


Figure 3: Experiment 1, 2, 4, and 5 simulation results. As the germanide gets thicker, the concentration of Co_5Ge_3 decreases and other phases form as indicated by the lighter colors of Co_5Ge_3

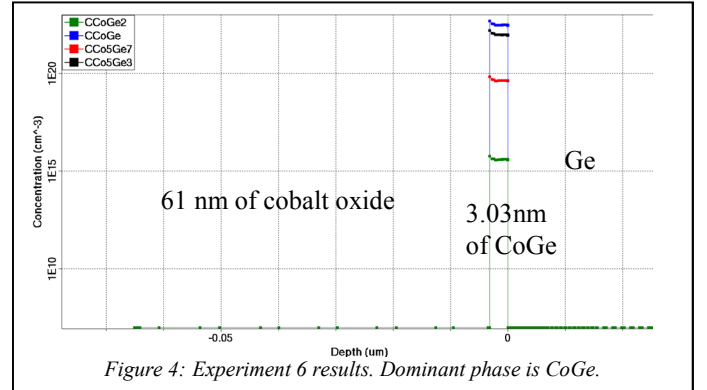


Figure 4: Experiment 6 results. Dominant phase is $CoGe$.

We are able to calibrate the reaction rates to fit the results of all the experiments in Table 1. k_2 , k_3 , and k_4 are responsible for forming the later phases. Calibrating their values to the different conditions reported in the literature allows us to obtain their temperature dependence. Their values are given in Table 3. k_1 is the reaction rate to form the first phase as well as the rate of growth of the cobalt germanide. In all the experiments in Table 1 the first phase has to form prior to forming other phases. We have not found reports of Co_5Ge_3 thickness as a function of time and temperature and there have not been many studies with long time anneals at different

temperatures. k_1 has been calibrated by considering the different germanide growth rates to satisfy the results detailed above for the 10 experiments.

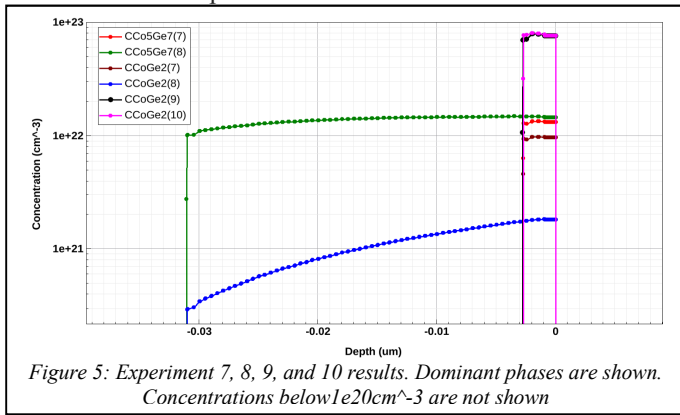


Table 2: Experimental parameters used in simulation

#	Temp. °C	Ambient	Time	Phase	Reference
1	227	Vacuum	24h	Co ₅ Ge ₃	[4]
2	227	Vacuum	48h	Co ₅ Ge ₃	[4]
3	250	Oxygen	1-20h	Co ₅ Ge ₃	[6]
4	250	Vacuum	1h	Co ₅ Ge ₃	[7]
5	220	Vacuum	1h	Co ₅ Ge ₃	[8]
6	227	Oxygen	48h	CoGe	[4]
7	400	Vacuum	1h	Co ₅ Ge ₇	[7]
8	457	Vacuum	1min	Co ₅ Ge ₇	[4]
9	600	Vacuum	1h	CoGe ₂	[7]
10	700	Vacuum	30min	CoGe ₂	[7]

Table 3: Simulation calibrated reaction constants.

Arrhenius equation	A (s ⁻¹)	E _a (eV)	Respective Co-Ge phase
k ₁	2e15	1.1	Co ₅ Ge ₃
k ₂	1.817e8	1.385	CoGe
k ₃	1.897e13	2.07	Co ₅ Ge ₇
k ₄	9.2695e9	1.972	CoGe ₂

CONCLUSION

The first multiphase kinetic TCAD model for cobalt germanidation was presented. The model parameters have been calibrated to experimental results reported in the literature. The model shows excellent agreement with experimental results and can explain all the results accurately. This model is an important process model for the design of cobalt germanide contacts.

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