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Citation: AIP Advances 7, 035214 (2017); doi: 10.1063/1.4978912
View online: http://dx.doi.org/10.1063/1.4978912
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Published by the American Institute of Physics

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Understanding the microwave annealing of silicon

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(Received 2 January 2017; accepted 7 March 2017; published online 15 March 2017)

Though microwave annealing appears to be very appealing due to its unique features, lacking an in-depth understanding and accurate model hinder its application in semiconductor processing. In this paper, the physics-based model and accurate calculation for the microwave annealing of silicon are presented. Both thermal effects, including ohmic conduction loss and dielectric polarization loss, and non-thermal effects are thoroughly analyzed. We designed unique experiments to verify the mechanism and extract relevant parameters. We also explicitly illustrate the dynamic interaction processes of the microwave annealing of silicon. This work provides an in-depth understanding that can expedite the application of microwave annealing in semiconductor processing and open the door to implementing microwave annealing for future research and applications. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

I. INTRODUCTION

Microwave annealing (MWA) has been reportedly used in organic synthesis, solid-state in organic materials, and the mixture of nanostructures and liquids, owing to its unique properties, such as volumetric, instantaneous, and material-selective heating. In recent years, MWA techniques have also been explored in semiconductor processing, including dopant activation in silicon, recrystallization of amorphous silicon films, silicide formation, preparation of reduced graphene oxide, processing of Ge-based metal–oxide–semiconductor field-effect transistors (MOSFETs) and In-Ga-Zn-O thin film transistors. These experiments report significantly lower temperature associated with MWA as compared with conventional thermal annealing (CTA) techniques, such as furnace annealing and rapid thermal annealing. However, its mechanism is yet not understood. The capability of low temperature processing makes MWA extraordinarily appealing, especially in the formation and activation of source/drain regions for future ultra-scaled MOSFETs in sub-14 nm nodes and emerging monolithic 3D sequential integrations. Hence, an in-depth understanding of the mechanism and an accurate model of MWA of Si are of paramount importance and urgency. The interaction of MWA with silicon can be categorized into thermal effects and non-thermal effects, the latter is still controversial to a certain extent. The thermal effects involve two major microwave heating processes: ohmic conduction loss and dielectric polarization loss. Though efforts have been made to characterize the effects of MWA in the processing of silicon integrated circuits, physics-based model and the rigorous derivation as well as explicit illustration of the dynamic interaction are still lacking. In this paper, we present the mechanisms of MWA processes in silicon and the relevant model.

Chaochao Fu and Yan Wang contributed equally to this work.

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Uniquely-designed experiments were employed for mechanism verification and relevant parameters calibration and extraction.

II. EXPERIMENTS

A p-type Si (100) wafer with a diameter of 200 mm, resistivity of 10.5 Ω·cm, and thickness of 725 µm was used in this experiment. After surface cleaning, the wafer was implanted with Ge with energy of 50 keV and dose of $1 \times 10^{15}$ cm$^{-2}$. As a result, an amorphous silicon layer of ~80 nm was formed, as shown in Fig. 1. The wafer was then sliced into square-shaped samples of 25 mm side-length. MWA was performed in a DSGI octagonal chamber at 5.8 GHz. During annealing, the samples were placed at the middle of the chamber, where the electromagnetic field is most uniform. The in situ temperature of the samples was monitored by a Raytek XR series infrared pyrometer facing the backside of the samples. Each sample was consecutively annealed three times. The samples were first annealed with one power condition, as shown in Table I, followed by a recrystallization anneal at 2800 W.\textsuperscript{5,24} The samples were further annealed using identical power conditions as the first annealing, as shown in Table I. Each annealing was 300 s with 5 min intervals between each in order to let the samples cool down to $T = 30$ °C. N$_2$ purged at a flow rate of 20 standard liters per minute was maintained throughout the whole MWA process.

III. RESULTS AND DISCUSSION

A. Ohmic conduction loss and dielectric polarization loss

The temperature profile for different MWA power levels is shown in Fig. 1. The peak temperature of the 280, 420 and 700 W samples in the post-recrystallization annealing process is lower

![Figure 1](image-url) 

**TABLE I.** Parameters for samples annealed at different microwave power.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>70</th>
<th>140</th>
<th>210</th>
<th>280</th>
<th>420</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$ (V/m)</td>
<td>1304.1</td>
<td>2684.8</td>
<td>5254.5</td>
<td>6042.8</td>
<td>8058.9</td>
<td>13093.3</td>
</tr>
<tr>
<td>$T_b$ (°C)</td>
<td>32.0</td>
<td>99.0</td>
<td>285.7</td>
<td>317.5</td>
<td>376.0</td>
<td>468.0</td>
</tr>
<tr>
<td>$T_a$ (°C)</td>
<td>32.0</td>
<td>98.7</td>
<td>280.0</td>
<td>310.4</td>
<td>362.4</td>
<td>451.3</td>
</tr>
<tr>
<td>$P_{abs,d}$ (Js$^{-1}$m$^{-2}$)</td>
<td>0.00</td>
<td>9.95</td>
<td>298.67</td>
<td>406.85</td>
<td>911.93</td>
<td>1457.46</td>
</tr>
<tr>
<td>$P_{abs,d} / E_0$ ($\times 10^{-5}$Js$^{-1}$V$^{-2}$)</td>
<td>0.00</td>
<td>0.14</td>
<td>1.08</td>
<td>1.11</td>
<td>1.40</td>
<td>0.85</td>
</tr>
</tbody>
</table>
than that in the pre-recrystallization annealing process (Fig. 1). However, the annealing conditions of the two processes are identical. This discrepancy can be explained by the lack of dielectric polarization loss (also calls dipolar polarization loss) in the post-recrystallization annealing samples, as the dipole defects (such as Frenkel pairs, vacancy-vacancy pairs, etc.) have been repaired during the recrystallization annealing process. Furthermore, ohmic conduction loss is the dominant microwave absorption mode during the post-recrystallization annealing process.

Both ohmic conduction loss and dielectric polarization loss exist during the pre-recrystallization annealing; hence, the equilibrium temperature for the annealing process before recrystallization \(T_b\) is higher than the corresponding temperature after recrystallization \(T_a\). However, when the microwave power is under 140 W, this temperature difference disappears. As the sample temperature is below \(\sim 100 \, ^{\circ}\text{C}\) under such low power annealing, the hopping frequency is extremely low compared to the microwave frequency, therefore not causing the dipole polarization loss. During the 300 s annealing, the sample’s absorption of microwave power is counterbalanced with heat radiation and convective-conductive heat transfer between the sample and the surrounding gas. The heat thermally conducting within the samples is ignored because the annealing time is long enough, and the temperature in the whole sample is uniformly distributed. Hence, the thermodynamic equilibrium equations for the pre-recrystallization annealing and post-recrystallization annealing are given as (see supplementary material):

\[
\begin{align*}
P_{abs-d} + P_{abs-o} &= \varepsilon\varrho T_a^4 + h_c(T_a - T_r) \\
P_{abs-o} &= \varepsilon\varrho T_b^4 + h_c(T_b - T_r)
\end{align*}
\]

When simplified, it becomes,

\[
P_{abs-d} = \varepsilon\varrho(T_a^4 - T_b^4) + h_c(T_a - T_b)
\]

where \(\varepsilon\) is the surface emissivity, \(\varrho\) is the Stefan-Boltzmann constant \((5.67 \times 10^{-12} \, \text{Js}^{-1}\text{cm}^{-2}\text{K}^{-4})\), \(h_c\) is the convective heat transfer coefficient \((25 \, \text{Js}^{-1}\text{m}^{-2}\text{K}^{-1})\), \(T_r\) is the temperature of purged \(\text{N}_2\) \((20 \, ^{\circ}\text{C})\), \(T_b\) is the equilibrium temperature for the pre-recrystallization annealing process, and \(T_a\) is the equilibrium temperature for the post-recrystallization annealing process.

Ohmic conduction loss and dielectric polarization loss are the two main modes of the absorption of microwave energy in silicon. Fig 2 illustrates ohmic conduction loss. The collision between electrons (or holes) and the silicon lattice induced by alternating the microwave electric field generates resistive heating, and hence transforms microwave energy into thermal energy.

The electric field and the angular frequency of the incident microwave are \(E_0\) and \(\omega\), respectively. For a sample with conductivity \(\sigma\) and thickness \(d\), the transformed microwave energy per unit area \(P_{abs-o}\) is:

\[
P_{abs-o} = \frac{1}{2} \int_0^d \int_0^1 \int_0^1 \sigma |E|^2 \, dx \, dy \, dz = \frac{\sigma E_0^2 |T_h|^2}{4\alpha} \left(1 - e^{-2\alpha d}\right)
\]

where \(\alpha = \sqrt{\omega \mu \sigma / 2}\), \(T_h = 2(1 + j)(1 + j + \eta_0 \sigma / \alpha)\) or the transmission coefficient of a normally incident wave at the interface of a lossy medium, \(\mu\) is the permeability of the target material, and \(\eta_0\) is the surface impedance of free space, \(\varrho = 5.67 	imes 10^{-12} \, \text{Js}^{-1}\text{cm}^{-2}\text{K}^{-4}\).

![Crystal lattice atom](image)

**FIG. 2.** Schematic representation of atomic and electron movements in a microwave field for ohmic conduction loss process, dielectric polarization loss process, and recombination process with Frenkel pairs (each consisting of an interstitial and a vacancy).
is the wave impedance of free space. Considering that microwave frequency is invariant for typical MWA tools, the ohmic conduction loss here is mainly dominated by the conductivity and thickness of the annealed samples. As the conductivity of semiconductors such as silicon and germanium changes with temperature, \(^1\) it is necessary to consider the temperature effect on the ohmic conduction loss process.

Dielectric polarization loss in silicon is mainly caused by dipole rotations during microwave annealing. The dipoles mainly exist in defect regions, which can be formed by, e.g. heavy implants into polycrystalline or single crystalline silicon and deposited amorphous layers. For example, in a Si layer that is heavily damaged via implantation, a high density of Frenkel pairs, vacancy-vacancy pairs, and other point defects would form.\(^\text{\(18\)}\) As interstitials tend to lose electrons and be charged positively, while vacancies tend to receive electrons and be charged negatively, \(^\text{\(19\)}\) each Frenkel pair or vacancy-vacancy pair can be regarded as a polarized dipole.\(^\text{\(5,14\)}\) The polarization model for the Frenkel pairs in a microwave field is schematically depicted in Fig. 2.\(^\text{\(20\)}\)

Two types of dipole rotations may happen during the polarization process: the interstitial rotates around the fixed vacancy, or vacancy rotates around the fixed interstitial. As interstitial or vacancy hopping is not rapid enough to build up a time-dependent polarization \(P\) that is in equilibrium with the electric field at any moment, this delay between electromagnetic stimulation and dipolar response is the physical origin of the dipolar polarization process in silicon.\(^\text{\(1\)}\) The polarization permittivity \(\varepsilon\) and its imaginary component \(\varepsilon''\) can be expressed as:\(^\text{\(21\)}\)

\[
\varepsilon = \varepsilon_0 (\chi + 1) = \frac{Nu^2}{12kT} \frac{1}{1 + i\omega\tau} + \varepsilon_0 
\]

\[
\varepsilon'' = \frac{Nu^2}{12kT} \frac{\omega\tau}{1 + \omega^2\tau^2} 
\]

where \(i = \sqrt{-1}\), \(\chi\) is the dielectric susceptibility, \(\varepsilon_0\) is the permittivity of free space, \(k\) is Boltzmann’s constant, \(T\) is temperature in Kelvin, \(N\) is the amount of dipoles per unit area, \(u\) is the dipole moment, and \(\tau = 1/(2\nu)\), where \(\nu\) is the hopping frequency of interstitial or vacancy.

Then the transformed energy for dipolar polarization per unit area \(P_{\text{abs-d}}\) is:\(^\text{\(16\)}\)

\[
P_{\text{abs-d}} = \frac{\omega}{2} \int_0^{\infty} \sqrt{\varepsilon} \cdot (iP) dV = \frac{\omega}{2} \int_0^{\infty} \varepsilon'' |\vec{E}|^2 dV = \frac{Nu^2}{24kT} \frac{\omega^2\tau}{1 + \omega^2\tau^2} E_0^2 
\]

where \(u = ql\), and \(q\) and \(l\) represent the charge and length of the dipole, respectively. The hopping frequency of interstitial or vacancy in silicon is expressed as:\(^\text{\(18\)}\)

\[
\nu = 10^{13} \exp \left( \frac{-E_b}{kT} \right) 
\]

where \(E_b\) is the diffusion barrier of interstitial or vacancy. The temperature therefore has a drastic influence on the hopping frequency of the interstitial and vacancy and, hence, the dipolar polarization process. This can well explain the observation that the silicon substrate temperature is an important factor for recrystallization and dopant activation by MWA.\(^\text{\(6,13\)}\) In order to fit the experimental data with the dielectric polarization loss model discussed above, equation (6) was transformed into:

\[
P_{\text{abs-d}} \frac{E_0^2}{E^2} = \frac{nu^2}{24kT} \frac{\omega^2\tau}{1 + \omega^2\tau^2} 
\]

The experimental data of \(P_{\text{abs-d}} / E_0^2\) (summarized in Table I and plotted in Fig. 3, with the curve calculated using equation (8)) for each annealed sample can be obtained and combined with the actual applied \(E_0\)\(^\text{\(15\)}\) for each microwave power in Table I. The fitting diffusion barrier \(E_b\) and \(Nu^2\) are 0.36 eV and \(1.6 \times 10^{-34}\) \(\text{C}^2\), respectively. 0.36 eV means that the interstitials take the dominant role of the dielectric polarization loss.\(^\text{\(26\)}\) Assuming the charge and distance for the dipole moment \(u\) is 4 electrons and 0.47 nm, \(N\) is \(1.7 \times 10^{17}\) \(\text{cm}^{-2}\). Considering the thickness of the amorphous silicon is \(\sim 80\) nm, the density of the dipole can be calculated as \(\sim 2 \times 10^{22}\) \(\text{cm}^{-3}\), which is slightly lower than the density of silicon (\(5 \times 10^{22}\) \(\text{cm}^{-3}\)). Reasonable extracted parameter values and fitting quality support the validation of the aforementioned theory and model.
It can be inferred that the key factors for microwave absorption via dielectric polarization loss are a high density of dipoles and proper substrate temperatures. In silicon, a high density of dipoles requires a high density of defects, which can be easily formed by implanting a high dose of heavier ions (As, BF$_2$, etc.). Pre-amorphization implantation using Ge or Si is another efficient way to achieve a high density of defects. Reaching the proper substrate temperature in a microwave chamber can be generated or accelerated using a susceptor wafer such as SiC or a silicon wafer with proper doping concentrations. Other measures, such as using a metal film covering, can assist silicon wafer heating. The metal covering can be heated significantly as a result of strong absorption of microwave energy via ohmic conduction loss in the material.

B. Non-thermal effects

In addition to the thermal effects discussed above, non-thermal effects also exist. According to the analysis above, the fitting diffusion barrier $E_b$ of silicon interstitials for microwave annealing is 0.36 eV, while the diffusion barrier is between 0.5-2 eV for traditional thermal annealing. This means that the diffusion barrier of interstitials and the combined barrier of interstitial and vacancy decreased in the microwave field.

According to Fig. 2, the average regrowth rate of the sample during recrystallization is calculated to be higher than 16 nm/min at $\sim$550 °C for a 2800 W microwave, while the regrowth rate is $\sim$10 nm/min for furnace annealing at the same temperature. This indicates so-called non-thermal effects, that the regrowth rate is increased with the assistance of the microwave field. Indeed, Sivalingam et al. and Fang et al. both found that the activation energy required for the bonding reaction by the microwave process is less than the thermal process, which leads to the recombination process being realized at lower temperature.

With the aforementioned results and discussion, the dynamics process in a complete cycle of MWA for implanted silicon can be identified and is shown in Fig. 4 (a). At the beginning of the annealing process, the heating energy is supplied dominantly by the ohmic conduction loss of the silicon substrate. The power of the dielectric polarization loss, which varies the hopping frequency of the interstitials in the amorphous layer, is much lower than the microwave frequency at room temperature. Along with the increase of the substrate temperature, the density of dipole polarization is greatly enhanced, causing a strong absorption of microwave energy in the amorphous layer via dielectric polarization loss.

Meanwhile, non-thermal effects also exist and play a role during the process of silicon recrystallization and defects repairation. When the recrystallization process is almost accomplished and defects are nearly repaired, both the non-thermal and dielectric polarization loss effects diminish. Meanwhile, the conductivity of the silicon wafer and the absorption power of the ohmic conduction loss vary until the substrate temperature reaches an equilibrium state. Consequently, such a self-limited heating process guarantees that the activated dopants are kept nearly frozen in the recrystallized region, hence leading to negligible dopant diffusion. With the analysis above, the temperature profile during
a complete annealing cycle for both MWA and CTA can be identified (Fig. 4(b)). MWA can significantly lower peak temperature and thermal budget for silicon recrystallization or defect-reparation annealing in less time.

IV. CONCLUSION

In summary, we have achieved an in-depth understanding and accurate model of MWA of Si in this paper. The mechanism and the physical model of the MWA of Si are proposed and experimentally verified for both thermal and non-thermal effects. The thermal effects involve two major microwave heating processes: ohmic conduction loss and dielectric polarization loss. Ohmic conduction loss is mainly influenced by the thickness and conductivity of the Si, which is dependent on the doped concentration and the actual temperature; dielectric polarization loss is mainly determined by the dielectric permittivity, which is dependent on the density of defects and the hopping frequency of interstitials, also influenced by the actual temperature. Non-thermal effects can be attributed to the enhanced probability and decreased activation energy associated with bonding reactions, and hence result in enhanced bonding reactions with the assistance of the microwave field. The self-limited process of silicon MWA during a complete MWA cycle is further explained by the dynamic evolution of both thermal and non-thermal effects. Hence, with its unique volumetric, material-selective and self-limiting heating features, together with the non-thermal effects, MWA has great potential to be used in Si and other semiconductor material processing. MWA may also be potentially solely adopted in future exotic applications whose demands match its unique capabilities.

SUPPLEMENTARY MATERIAL

See supplementary material for more information on the thermal equilibrium equation.

ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (61474028) and National S&T Project 02 (2013ZX02303-004).