INTRODUCTION

Continued shrinkage of silicon device dimensions and increasing complexity of device processing has led to an increase in stress levels in the active regions of silicon devices. The stress can alter diffusion kinetics of implanted dopants and in some instances lead to the formation of extended defects. The primary goal of this study is to investigate the effects of stress on dopant diffusion and extended defect evolution. In addition, a quantitative model, which can be used to predict the effect of stress in more general situations, is developed and implemented into a process simulator.

Investigations of several researchers have revealed that phosphorus and boron exhibit retarded diffusion when annealed under a deposited nitride layer. As early as 1982, Mizuo and Higuchi observed anomalous diffusion of boron and phosphorus in silicon under chemical vapor deposited (CVD) nitride films. They discovered that in an inert atmosphere the diffusion of these dopants under CVD nitride films is retarded compared to the diffusion under the SiO$_2$ films covered with CVD nitride. Their results indicated that the Si–SiO$_2$ interface could be acting as a sink for supersaturated interstitials. However, they neglected the high levels of stress in the nitride film, and theorized that the deposited nitride film was inert, with regards to perturbing point defect concentrations in the bulk. Ahn et al. observed a vacancy supersaturation and a self-interstitial undersaturation under low pressure chemical vapor deposited (LPCVD) nitride with tensile stress. The degree of super or undersaturation of point defects was found to be closely related to the stress level in the silicon nitride film. They further theorized that the nitride film was generating vacancies by absorbing silicon atoms at the interface to relieve its own tensile stress. Osada et al. investigated the effect of an LPCVD nitride on boron diffusion in the substrate below. They observed that as long as the nitride thickness was greater than 50 Å, boron diffusion was retarded under the nitride film, when compared to a region where an oxide film was under an overlying nitride. In addition, this retardation in boron diffusion was found to increase with increasing nitride film thickness and decreasing anneal temperature. The results were explained solely due to compressive stress in the substrate below the tensile deposited film, which lead to an undersaturation of vacancies. Kuo et al. investigated boron diffusion in Si and Si$_{1-x}$Ge$_x$. They observed slower boron diffusion in compressively strained Si$_{1-x}$Ge$_x$, when compared to unstrained silicon, and attributed it to an increase in interstitial formation energy in the compressive Si$_{1-x}$Ge$_x$. However, the intrinsic boron diffusivities in Si$_{0.80}$Ge$_{0.20}$ and Si$_{0.90}$Ge$_{0.10}$ exhibited weak strain dependence, suggesting that the boron diffusivity in Si$_{1-x}$Ge$_x$ is predominantly a function of Ge content.

Since both phosphorus and boron diffuse mainly through an interstitial mechanism, it has been suggested that the compressive stress in the substrate immediately below the tensile nitride layer leads to an undersaturation of interstitials, which would explain the retarded diffusion. The research, described in the preceding paragraph, suggests that the stress in the nitride film has a significant effect on bulk diffusion properties. A comprehensive look at the diffusion properties of a representative dopant, as a function of film thickness and stripe width, would not only greatly enhance the understanding of stress-assisted diffusion, but also allow the calibration of process simulators like Florida object oriented process simulator (FLOOPS). FLOOPS allows simulation of semiconductor device processing in one, two, or three dimensions. It uses finite element analysis to determine the magnitude of stress from sources such as deposited films. These simulations are quite accurate as they use the standard finite element technique to solve the balance of forces equation. However, the effect of a given stress field on variables such as dopant diffusivities needs to be calibrated. In order to facilitate such calibration, an experiment is designed to introduce stress in the silicon substrate in a predetermined way. Finite element stress simulations in FLOOPS (Fig. 1) revealed that patterned nitride films introduce both compressive and tensile stress in the substrate. The stress levels in the substrate are a strong function of nitride film thickness and stripe width. Thus, such structures would be extremely use-
An experimental procedure is designed to investigate the effects of stress on the evolution of dislocation loops and on the diffusion of phosphorus as a representative dopant. A series of nitride stripes are used to generate alternating tensile and compressive stress fields in the substrate. The diffusion of phosphorus under the masked and unmasked regions is compared using the standard junction staining technique. The evolution of the dislocation loops with anneal time is monitored using the transmission electron microscopy (TEM) technique. Although both the phosphorus diffusion and dislocation loop experiments were performed in parallel, for the sake of clarity the results are discussed in separate sections.

II. EXPERIMENTAL DETAILS

*p-type* boron doped (15–25 Ω cm resistivity) Czochralski (100) oriented wafers were used for the study. The wafers were annealed in dry oxygen for 60 min to grow a 300 Å oxide. Ellipsometric measurements were utilized to confirm that the thickness of the oxide did not appreciably change on the same wafer as well as from wafer to wafer. The oxide initially served as a screen from ion implantation and subsequently as a diffusion mask to prevent loss of dopant during annealing. A Varian ion beam implanter was used to implant phosphorus into half the silicon wafers through the screen oxide. High dose diffusions effects during the subsequent anneal were eliminated by utilizing a dose (1 × 10^{14}/cm²) below the amorphizing threshold of silicon. The energy of the implant (100 keV) was chosen to match standard implantation procedures in modern complementary metal oxide semiconductor (CMOS) processes. Under these implant conditions the dopant redistributed itself in a 1-μm-deep region in the silicon substrate. This would aid subsequent cleaving of the samples for junction measurements. The wafers were then subjected to a 30 min/900 °C anneal to remove the implantation damage and activate the implanted dopant. The second set of wafers received a silicon implant (1 × 10^{13}/cm², 50 keV). The implant conditions were chosen so as to amorphize the substrate to a depth of ~1300 Å. During subsequent anneals type-II dislocation loops would be formed at this depth.

A spin on technique (3500 rpm/25 s) was used to deposit an I-line photoresist on the oxide coated wafers. A photolithographic stepper then patterned stripes ranging in width from 1–1000 μm on the photoresist. Using the photoresist as a mask, a 10:1 buffered hydrofluoride etch was employed to create corresponding stripes in the oxide layer. The lateral etch was insignificant since the thickness of the oxide was 0.03 μm. The remaining photoresist was then removed by boiling the wafers in 110 °C solution of sulfuric acid and hydrogen peroxide.

A LPCVD silicon nitride was deposited on the wafers to generate the stress in the substrate. The nitridation was performed at 900 °C/211 mTorr. The following flow rates were used for the various gases during the process; nitrogen: 48 sccm; SiHCl₃ :60 sccm; Ammonia: 882 sccm. The flow rates were chosen to match stress calibrated nitrides found in the literature. Under these conditions it is estimated that the

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**FIG. 1.** Finite element simulation of the hydrostatic pressure under a nitride stripe in FLOOPS illustrating the regions of compression (under nitride) and tension (under the oxide padded nitride).

**FIG. 2.** A representative diagram of a metal oxide semiconductor field-effect transistor (MOSFET) with its possible isolation schemes, showing the location of dislocation loops and dopants. A, B, and C are the possible sources of stress that may influence the evolution of dislocation loops or the diffusion of dopants.
The angle was chosen in view of the fact that the predominantly cut into technique to demarcate the junctions. The samples were initially cut into ~3 mm square pieces. They were mounted on a stainless steel chuck with a cleaving angle of ~17 min. The angle was chosen in view of the fact that the predominant stress levels in the nitride are of the order of $1 - 5 \times 10^9$ dynes/cm². Simulations in FLOOPS suggest that this would generate sufficient stress in the silicon substrate to observe the effects under investigation. The stress levels, however, would remain below the yield strength of silicon. The phosphorus samples were then annealed in a nitrogen ambient at 1000 °C for times ranging from 2 to 4 h. The silicon implanted samples were annealed at a lower temperature (900 °C) to prevent rapid dissolution of the dislocation loops. A flow chart depicting the entire experiment is shown in Fig. 3. The phosphorus samples were analyzed using the junction staining technique, while TEM was employed to investigate the evolution of dislocation loops. The two techniques are briefly described in the subsections below.

### A. Junction staining

As discussed earlier compressive stress below the nitride stripes and tensile stress outside the stripes would alter the diffusion kinetics of the dopant. Since the dimensions of the stripes range from 1 to 1000 μm a convenient method to quantify the diffusion would be to use a junction staining technique to demarcate the junctions. The samples were initially cut into ~3 mm square pieces. They were mounted on a stainless steel chuck with a cleaving angle of ~17 min. The angle was chosen in view of the fact that the predominant diffusion is within a micron of the surface. A diamond compound on a glass plate was used as the grinding surface. Upon cleaving a chemical stain was used to demarcate the n-type dopant. The samples were placed under an optical microscope and two junction depths (one representing the diffusion under the nitride film, and the other representing diffusion under the oxide/nitride films) were measured for each sample using the micrometer scales on the microscope.

### B. Transmission electron microscopy

The silicon implanted samples were mechanically lapped and jet etched for observation under a JEOL 200CX TEM. The analysis was performed using weak-beam dark field ($g_{220}$) image of the samples. By measuring loop size and their numbers in plan view, it was possible to determine quantitatively the total density of the loops, their radii, and the concentration of atoms trapped in the loops. Assuming a circular loop, the radius of each loop was measured along its longest axis and the corresponding loop area was calculated. The concentration of atoms bound by the loops is estimated by multiplying the fraction of the loop area by the atomic density in the (111) plane ($1.5 \times 10^{15}$/cm²).

### III. EXPERIMENTAL RESULTS

Experimental results from the phosphorus and silicon implanted samples are discussed in the Secs. III A and III B. Since phosphorus diffuses mainly through interstitials, Sec. III A brings out the effect of nitride stripes on point defects. Section III B elucidates the effect of identical nitride stripes on extended defects (ion-implanted dislocation loops).

#### A. Phosphorus implanted samples

Figure 4 illustrates the effect of the nitride stripes on the diffusion of phosphorus in silicon, which is quantitatively represented as $\Delta X_j$. It is the difference between the junction depth under a nitride stripe (i.e., the region where the nitride is directly on top of the silicon) and outside it (i.e., the region where an oxide layer is padded between the nitride layer and the silicon substrate). The trends are quite apparent. As the thickness of the nitride layer is increased, the net retardation ($\Delta X_j$) increases. An increase in the stripe width for the same nitride thickness also causes $\Delta X_j$ to increase.

#### B. Silicon implanted samples

Two fundamental figures of merit used to quantify a dislocation loop ensemble are its total density ($D_{\text{total}}$) and the average radius ($R_{\text{ave}}$). Earlier work quantified their evolution in an inert ambient. This study focuses on the net variation in these quantities from region A to region B (Fig. 1). Figure 5(a) shows a dark field plan view TEM microphotograph under the compressed region (region B) of a 20 μm stripe width sample. Figure 5(b) is a similar plan view under the tensed region (region A) of the same sample. The thickness of the nitride film is 1000 Å, and the sample was annealed for 90 min at 900 °C. The loops are consistently found to be sparser and smaller under a nitride layer, i.e.,

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**FIG. 3.** Flow schematic of the experiment designed to study the effect of nitride stripes on the diffusion of phosphorus and evolution of ion-implanted dislocation loops in silicon.
where $D_{\text{all}}$ is the total density of loops, and $R_{\text{ave}}$ is the average radius of the loops.

**IV. DATA ANALYSIS AND MODELING**

The effects of patterned nitride films on the diffusion of phosphorus and the evolution of dislocation loops were experimentally investigated in the previous sections. The diffusion of phosphorus was retarded in regions of compression and enhanced in regions of tension. The dislocation loops were found to be sparser and smaller in regions of compression when compared to the adjacent tensile regions. The experimental results are analyzed and modeled in Secs. IV A and IV B.

**A. Simulation of the stress-assisted diffusion of phosphorus**

Tensile stress is known to exist in the LPCVD deposited nitride film.\textsuperscript{5} This stress leads to a compressive stress field immediately below the nitride film (finite element stress simulations in FLOOPS—Fig. 1). In the regions where an oxide film pads off the overlying nitride film the substrate is under tension. The equilibrium concentration of point defects is changed by the presence of this stress field, and is quantitatively represented as

\begin{equation}
C_I^0(P) = C_I^0(P=0) \exp \left( \frac{-P \Delta V_I}{kT} \right),
\end{equation}

\begin{equation}
C_V^0(P) = C_V^0(P=0) \exp \left( \frac{P \Delta V_V}{kT} \right),
\end{equation}

where $C_I^0(P)$ is the equilibrium concentration of interstitials/vacancies in the presence of the pressure field, $P$ is the spatially dependent magnitude of the pressure field, $k$ is the Boltzman’s constant, and $T$ is the temperature. $\Delta V_I$ and $\Delta V_V$ are effective interstitial and vacancy expansion volumes, and are defined as

\begin{equation}
\Delta V_I = 1.33 \pi r_o^3,
\end{equation}

\begin{equation}
\Delta V_V = 2 \pi r_i^2 \gamma \Gamma / \mu,
\end{equation}

where $r_o$ and $r_i$ are the radius and dilatation of the dopant atom, $r_s$ and $\Gamma$ are the radius and surface tension of the vacancy well, respectively, $\mu$ is the shear modulus of silicon, and $\gamma$ is related to the Poisson’s ratio $\eta$ of the material ($=0.3$ for silicon) as
Stress simulations in FLOOPS suggested that increase in the thickness of the deposited nitride layer would lead to higher levels of stress in the substrate below the layers. This explains the added retardation observed in the experimental data as the thickness of the nitride layer was increased. These results do not qualitatively agree with the data of Ahn et al.\(^2\)

\[
\gamma = 3.0 \cdot \frac{1 - \eta}{1 + \eta} \quad (7)
\]
In their study the retardation was found to remain constant with an increase in thickness of the nitride layer. It should be noted that the stress in the nitride film is strongly dependent on the deposition conditions, which are different in the two experiments. However, they did observe a marked decrease in the net retardation as the width of the stripe was reduced, which concurs with the results of this study.

An increase in width of the nitride stripes, with the thickness remaining the same, leads to a decrease in the stress levels in the substrate in regions close to the interface. This was corroborated by FLOOPS simulations (Fig. 6). Therefore, with a tensile intrinsic stress in the nitride film, it is expected that the compressive pressure immediately below the nitride stripe would increase as the stripes are brought closer together (i.e., made smaller). This would decrease the local equilibrium concentration of interstitials in the region immediately below the nitride layer. Since phosphorus is known to diffuse mainly through an interstitial phenomenon, it is expected that the net retardation (\(\Delta X_j\)) would increase as the stripes are made smaller and brought closer together. The results of this study, however, suggest some competing phenomena is at work. A first order analysis of this phenomenon is presented in the subsequent paragraph.

The stripe width dependent stress analysis presented in the preceding paragraph is true for regions that are very close to the silicon/nitride or silicon/oxide interface. For regions deeper in the substrate, the stress levels increase with increasing stripe width (Fig. 6). Since the junction staining technique is sensitive only to the junction depth in the sample, this competing mechanism is responsible for the increase in the net retardations with increasing stripe width.

For the 1 \(\mu\)m stripe width samples the net retardation (\(\Delta X_j\)) falls to \(~400\) Å, and is at the resolution limit of the junction staining technique. For the widest stripes (1000 \(\mu\)m), the retardation increases almost threefold, to \(~1300\) Å.

The effect of a stress field on the local concentration of point defects is described by Eqs. (3) and (4). Thus, if a dopant-like phosphorus (known to diffuse mainly by an interstitial mechanism) is annealed in the presence of the nitride stripes, it should show a retardation in diffusion in regions of compression. While simulating the stress-assisted diffusion of phosphorus it is also important to incorporate the effect of the stress on the binding energy of the dopant-defect pair. The binding energy of a point defect pair is defined as the difference in the thermodynamic potential of the paired and unpaired point defect. Physically, the binding energy determines the number of point defect pairs that are present in the bulk. For the zero stress case, the binding energy is a constant dependent only on temperature. For the case when a nonzero stress field exists, the binding energy becomes dependent on the stress at any given location in the substrate. This makes the pairing coefficient a spatially varying quantity; the total number of point defect pairs in equilibrium are written\(^8\) as

\[
C^*_{AX(p)} \equiv C^*_{AX(p=0)} \exp \left( -\frac{P \Delta V_{AX}}{kT} \right),
\]

where \(P\) is the hydrostatic pressure, and \(\Delta V_{AX}\) are the effective volumes for elastic inclusion of dopant point defect pairs. Mathematically, it is positive for the interstitials and negative for the vacancies. Thus, the equilibrium concentration of phosphorus-interstitial pairs decreases, and phosphorus-vacancy pairs increases in a compressive medium. The model predicts a retardation in the diffusion of phosphorus in a compressive medium. The change in the point defect and dopant-point defect pair concentrations need to be simultaneously accounted for while simulating the stress-assisted diffusion of phosphorus.

Equation (8) brings out the effect of a stress field on the dopant-point defect pairs in the substrate and is implemented in FLOOPS by making the pairing coefficient a function of the pressure:

\[
K^C_{AX(p)} = K^C_{AX(p=0)} \exp \left( -\frac{P \Delta V_{AX} + P \Delta V_X}{kT} \right),
\]

where \(\Delta V_{AX}\) and \(\Delta V_X\) are positive for interstitials and negative for vacancies. Equation (9) implicitly accounts for the physics in Eq. (8). These equations are strongly sensitive to the effective volumes of the point defect and dopant-point defect pairs.

Under the annealing conditions used in the experiment, simulations showed that the effect of Eqs. (3), (4), and (9) on the diffusion of phosphorus is comparable. The volumes are extracted assuming the silicon interstitial to be a hypothetical sphere with radius equal to half the radius of single silicon atom. This is an approximation of the exact value, which should be the radius of the cavity into which the “self-interstitial” is inserted. For the vacancy volume, the effective radius \(r_v\) is assumed to be exactly equal to the radius of the missing atom. The value used for \(\Delta V_{PI}\) is estimated from
the radius of a hypothetical sphere with radius equal to the sum of the radii of a phosphorus atom and a silicon self-interstitial. The corresponding volume for a dopant-vacancy pair is more complicated to estimate, and is assumed to be twice that of the dopant-interstitial pair. Since the phosphorus diffuses almost entirely via an interstitial mechanism, the results of the simulations showed a weak dependence on the dopant-vacancy inclusion volumes. The stress levels in the nitride film are modified to account for the thermal strain at 1000 °C. The results of the simulations are directly compared with the experimental data in Fig. 4. The error bars for the measured data in the figure have been extracted by staining multiple samples from the same experimental split. This yields the bounds for the measured data. The discrepancy between the simulated and measured data points for the 20 y yields the bounds for the measured data. The discrepancy between the simulated and measured data points for the 20 μm/2 h sample in Figs. 4(a) and 4(b) is of the order of 50–100 Å, and is probably due to experimental error.

B. Simulation of stress-assisted evolution of dislocation loops

A model for the evolution of dislocation loops in an inert ambient, based on the Ostwald ripening phenomenon has been developed. The loss or gain of atoms during the anneal was found to be a strong function of loop size. Loops above a certain critical radius gained atoms and grew in size, while loops below the same critical radius lost atoms and eventually dissolved. This loss or gain of atoms for a given loop was also strongly dependent on the concentration of point defects in the bulk at its edge. In the presence of a pressure field the point defect concentrations are defined by Eqs. (3) and (4).

The continuity equation for the loss or gain of atoms for a loop with radius \( R \) can now be rewritten by including the pressure dependence as

\[
\frac{\partial n}{\partial t}_{\text{at Radius } R} = \alpha K_{IL}[C_I(P) - C_{IL}] - \alpha K_{IV}[C_V(P) - C_{IV}]_{\text{at Radius } R}
\]

where \( \alpha \) is an effective cross section of the loop layer in the unit of linear length, \( K_{IL} \) is the constant of reaction between the interstitials and the dislocation loops, \( K_{IV} \) is a similar constant for vacancies, \( C_{IV}(P) \) is the concentration of interstitials/vacancies in the presence of the pressure field, and \( C_{IV/Vb} \) is the number of interstitials/vacancies that a given dislocation loop can support at its edge.7,9

In the presence of a pressure field the equilibrium concentration of point defects would change, altering their concentrations in the bulk, i.e., \( C_{IV}(P) \) is a function of pressure. Thus, Eq. (10) has an implicit pressure dependence. This implies that the rate of growth of the loops is now spatially dependent, dictated by the pressure field. To illustrate this point, assume that the pressure in a given region is compressive. The quantity on the left in Eq. (10) would decrease and, therefore, reduce the rate of growth of loops in that region. Similarly, the average rate of growth of loops in a tensile region would increase. This agrees qualitatively with the results of the experiment. Other loop ensemble properties, such as the maximum and minimum radius, and total loop density, change in accordance with the model described. Since the anneal was done at 900 °C, the parameters extracted7 are used again for the simulations.

The general procedure for characterizing dislocation loop ensembles in silicon has been discussed in detail. The peak radius \( R_{\text{peak}} \), average radius \( R_{\text{ave}} \), the density of loops with peak radius \( D_{\text{peak}} \), and the total density of loops \( D_{\text{all}} \), were used to characterize a dislocation loop ensemble. This procedure works well if the objective is to quantify the time evolution of a dislocation loop ensemble. However, in this experiment the goal is to investigate the stress-assisted evolution of dislocation loops. In particular, the focus is on the change in the properties of the loop ensemble from regions of compression (region B) to regions of tension (region A). To explain the effects observed in the experimental data the following three quantities are defined:

![Graph](image_url)
The trend for the change in point-defect elastic inclusion volumes.

As the stripes are brought closer together the net variation in the total density of the dislocation loops increases (for most cases), while the net variation in the average loop radius diminishes. Though the variation in $\Delta D_{\text{all}}$ is within error bars, the trend for the change in $\Delta R_{\text{ave}}$ and $\Delta N_{\text{trap}}$ is quite evident. As the stripe width is increased the stress level in regions immediately below (<0.5 µm) the silicon surface decreases (Fig. 6). This is reflected in the stripe width dependence of the loop ensemble properties ($\Delta R_{\text{ave}}$ and $\Delta N_{\text{trap}}$).

These results are consistent with the hypothesis in the previous section: a compressive stress field in region B forces an increase in the equilibrium concentration of vacancies. Under these conditions an interstitial inside the loop is more likely to leave the ensemble and recombine with a vacancy outside the loop, or a vacancy might move into the loop and cause it to shrink. A reverse phenomenon is in effect in region A, which leads to bigger and denser loops in that region.

C. Validity of extracted volumes

The diffusivities of the dopant and point defects used for the simulations are their default values in FLOOPS. The effective volumes used for the simulations are consistent with Park et al. Since there is an exponential dependence of the bulk processing variables on these volumes, it is necessary to examine the validity of these parameters with the results of other researchers. This section examines the validity of the model and the methodology for extracting the effective dopant point-defect elastic inclusion volumes.

Osada et al. observed retarded diffusion of boron, when annealed under deposited nitride films. They suggested that a tensile stress of $\sim 1 \times 10^9$ dynes/cm² in the film was compressing the silicon below, thereby retarding the diffusion of the dopant. Although the effective volumes for the point defects are the same as the ones described earlier, the effective volumes for the dopant-point defect pairs are different for boron. To be consistent with the assumptions made while simulating the stress-assisted diffusion of phosphorus, the value used for $\Delta V_{BI}$ is estimated from the radius of a hypothetical sphere with radius equal to the sum of the radii of a boron atom and a silicon self-interstitial. The corresponding radius for a boron-vacancy pair is assumed, as before, to be twice that of the dopant-self-interstitial pair.

The results of the simulations are shown in Fig. 9. The implanted dopant is boron (70 keV, $7.5 \times 10^{13}$/cm²) and the anneal is performed at 1014 °C for 2 and 6 h. The net retardation from the simulations matches well with the data from Osada et al. The experimental data indicate the absence of relaxation in the stress in silicon with time. This is probably because a major component of the stress is due to the thermal mismatch between the nitride and silicon substrate. This stress is present as long as the anneal temperature is maintained at 1014 °C.

V. CONCLUSION

The behavior of point defects under varying stripe widths of a nitride layer has been indirectly studied by observing the diffusion of phosphorus. The diffusion of phosphorus is retarded under regions where the nitride film is directly on top of the silicon substrate when compared to phosphorus diffusion in regions where an oxide pads off the silicon substrate from an overlying nitride film. As the stripes are made narrower and brought closer together this...
net retardation decreases in magnitude. The anomalous diffusion is shown to be consistent with finite element stress and diffusion simulations.

The number of trapped atoms in a dislocation loop ensemble under a nitride film is found to be lower when compared to a region where the oxide layer pads off the underlying silicon substrate from the nitride film. As the stripes are made narrower and thus brought closer together the magnitude of this difference increases. The loops are always sparser and smaller under a nitride film. This anomalous behavior is consistent with the stress and loop evolution simulations in FLOOPS.

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