Template-Directed Self-Assembly of Buried Nanowires and the Pearling Instability

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The fabrication of more and more miniaturized electronic and photonic devices relies on new, ingenious methods for the fabrication of spatially controlled nanostructures. Examples are electronic devices based on semiconducting nanowires and photonic devices based on chains of metallic nanoclusters that guide light by coupled surface plasmons. In this contribution a template-directed ion beam synthesis of nanowires and regular nanocluster chains will be presented. As templates, V-grooves etched in (001)Si and subsequently oxidized are used. High fluence Ge$^{+}$ implantation is carried out into the SiO$_2$ layer at 70 keV. Thereby, the implanted Ge enriches themselves in the V-groove bottom to a critical amount, which may result in nanowire formation by nucleation, growth and coalescence during subsequent thermal treatment. TEM investigations indicate the formation of a nanowire buried in the SiO$_2$ at the V-groove bottom.

Kinetic lattice Monte Carlo simulations of the nanowire formation process were performed in order to understand the phase separation mechanism and results are compared to TEM images. Furthermore, it is shown that even ideal nanowires show an instability and form during long-lasting annealing equal-spaced and equal-sized nanoclusters (“nanocluster chains”) by self-organization.

I. INTRODUCTION

A wide field for novel applications opens at the bottom of the length scale accessible by modern semiconductor preparation techniques. Synthesized nanostructures show interesting physical properties being completely different from the bulk material. Besides other applications, this could help to miniaturize modern optical devices. Thus, having metallic nanoclusters arranged in a regular chain, light can be transported by the coherent coupling of surface-plasmon-polaritons [1]. Along such a chain, light can be guided around corners well below the classical diffraction limit, allowing the integration of optical devices on the chip-level (Plasmonics) [2].

However, the precise synthesis of the nanostructures needed for such applications remains a great challenge to current research. This becomes even more important since classical structuring fails at this level. Here, self-organization processes might be able to assemble structures with nanometer dimensions. In particular, the ion beam synthesis (IBS) became successful for fabrication of buried nanostructures. Quantum dots were formed under various conditions [3, 4]. Using very high ion fluences, buried layers were synthesized [5].

In order to obtain spatially well-defined nanostructures, taming of self-organization of pattern formation is an attractive approach. In the present contribution, this is achieved by oxide covered Si V-grooves as templates, which guide the self-assembly of buried nanowires from implanted Ge atoms during thermal treatment. This scheme is depicted in Fig. 1. By a similar approach Si nanowires were recently fabricated by O$^+$ implantation into Si V-grooves [6]. However, the method of ref. [6] is restricted to Si wires and is hard to control. Here, Ge was implanted as it is a well-known material for nanocluster synthesis. However, also other ions can be easily applied, e.g. Au for plasmonic devices. Different stages of the fabrication process were monitored by cross sectional Transmission Electron Microscopy (X-TEM) investigations.

Theoretical studies are presented to understand details of the phase separation mechanism. On the atomic scale, within kinetic 3D lattice Monte Carlo simulations (KLMC), the diffusion of Ge atoms, their nucleation to clusters, cluster ripening and coalescence are tracked. For long lasting thermal treatment such simulations also describe the pearling instability of wires. A nanowire tends to decay into droplets driven by the minimization of interfacial energy and highly regular chains of equal-sized and equal-spaced nanoclusters form.

![FIG. 1: Scheme of the ion beam synthesis of a buried Ge nanowire at the bottom of an oxidized silicon V-groove. (a) Ge$^+$ ions are implanted at high fluence into the V-groove. Atoms are sputtered from and are redeposited onto the sidewalls leading to a mass transport towards the V-groove bottom. During annealing (b) in an inert ambient a nanowire may form at the V-groove bottom.](image-url)
II. EXPERIMENTS

V-grooves aligned along the [110] direction on (001)Si wafers were prepared by photolithographic masking and anisotropic etching with 30% KOH at 80 °C. This self-adjusting process results in atomically smooth (111) crystal facets forming the sidewalls of the V-grooves with an angle of 54.7 ° to the plane wafer surface. V-grooves of 4 µm width and 5 mm length were studied. They were oxidized in dry O₂ at 1000 °C, leading to 200 nm thick SiO₂ on the (001)Si surface and 220 nm thick SiO₂ on the (111) sidewalls of the V-groove. A sharp surface depression forms during oxidation at the V-groove bottom, which can be seen in X-TEM images (Fig. 2 a). The SiO₂ covered V-grooves were implanted at room temperature with $1 \times 10^{17}$ Ge⁺ cm⁻² at 70 keV (flux density $3 \times 10^{12}$ cm⁻² s⁻¹). The content of Ge in the SiO₂ appears thereby as dark shadow in the TEM image (Fig. 2 b). During implantation, Ge is enriched in the V-groove bottom compared to the sidewalls due to (i) the reduced ion density per surface area at the sidewalls caused by the inclination and (ii) due to ion erosion of the sidewalls. Sputtered atoms including Ge are redeposited at the opposite sidewall and refill the sharp kink at the as-oxidized V-groove bottom. The V-groove surface evolution under ion bombardment was recently modeled in a continuum framework in nice agreement with V-grooves shapes observed in TEM images also proving a Ge accumulation of 30% in the V-groove bottom.

Subsequent furnace annealing in N₂ ambient was performed at 950 °C for 10 minutes. Thereby, the small amount of implanted Ge is extremely sensitive to moisture, which may result in the oxidation of Ge. Therefore, (i) the standard wet cleaning step in H₂O₂/H₂SO₄ prior to any thermal processing was skipped and (ii) the samples were transferred into the cold furnace and then purged in cold N₂ in order to reduce the moisture intake. Fig. 3 shows an XTEM image of an annealed sample. Buried Ge clusters are present in the sidewalls and the bottom. The dark dot, visible in the V-groove bottom, is a cross-section of the expected nanowire with a diameter of 35 nm. All Ge cluster are crystalline, which is confirmed by a high resolution TEM image, Fig. 4, of a Ge cluster showing lattice fringes.

The continuity of the wire over long distances remains to be proven. Several XTEM images taken from different cross-sections show always the large black dot with identical diameter and position in the V-groove bottom, which is an indication for a continuous nanowire.

III. KINETIC MONTE-CARLO SIMULATIONS

KLMC simulations were performed in order to understand the wire formation from dispensed Ge

![FIG. 2: XTEM images of (a) an as-oxidized and (b) an as-implanted sample (70 keV, $1 \times 10^{17}$ Ge⁺ cm⁻²). The Ge content in the SiO₂ appears as dark shadow in the TEM image (b).](image2)

![FIG. 3: XTEM image of an annealed sample. The large dark spot in the V-groove bottom appears to be a cross section of a Ge nanowire with 35 nm diameter.](image3)

![FIG. 4: High resolution TEM image of a Ge cluster in an annealed sample showing lattice fringes, which proves the crystallinity of the precipitates.](image4)
The binding energy interaction is assumed to be configuration independent. For diffusion, the most simple implementation is used, i.e. the in-energy for a transition probability to an arbitrary empty nearest-neighbor site with the predecessor by a jump of a randomly chosen Ge atom is successful ($E_A$). Additionally, the diffusion of Ge monomers in the host matrix is thermally activated with an activation energy $E_A$.

Then, the transition from the initially out-of-equilibrium state to the thermodynamically equilibrium state is described by the importance sampling of configurations according the Metropolis algorithm. A sequence of states is produced representing the time evolution, where each state is generated from its predecessor by a jump of a randomly chosen Ge atom to an arbitrary empty nearest-neighbor site with the transition probability

$$P_{if} \sim \begin{cases} \exp \left\{ -\frac{E_A}{k_BT} \right\}, & n_f \geq n_i, \\ \exp \left\{ -(n_i - n_f) \frac{E_A}{k_BT} - \frac{E_B}{k_BT} \right\}, & n_f < n_i. \end{cases}$$

During one Monte Carlo step (MCS) each atom performs statistically one attempt to jump from its initial site $i$ to a final site $f$. Thereby, the activation energy for diffusion $E_A$ is assumed to be the same for each possible transition, i.e., for interface and bulk diffusion. Thus, it is possible to renormalize the transition probability $P_{if}$ such that each diffusional jump is successful ($E_A \to 0$), which only scales the time of a MCS thereby improving the simulation speed

$$P_{if} \sim \begin{cases} 1, & n_f \geq n_i, \\ \exp \left\{ -(n_i - n_f) \frac{E_A}{k_BT} \right\}, & n_f < n_i. \end{cases}$$

This approach has been proven useful for the description of precipitation after ion implantation and the evolution of fcc surfaces under ion erosion.

For the KLMC simulations of the nanowire formation a simplified initial distribution of Ge atoms was assumed. A cylindrical profile with a Gaussian cross section aligned to the [100] direction of the simulation lattice was used (Fig. 5) with a peak concentration of 31% and 4 nm standard deviation. 95% of the implanted atoms lay in a cylinder of 16 nm diameter, which resembles the Ge-rich region at the V-groove bottom, see Fig. 5b).

During annealing, Ge nanocluster nucleate from the supersaturation and grow in time. They mostly have nucleated at the position of highest supersaturation, which is the profile center. As they grow, they start to touch each other and coalesce to extended structures. A continuous wire forms if this coalescence proceeds further, while the surrounding nanoclusters evaporate and Ge condenses onto the wire-like structure, see Fig. 5b,c). The complete coalescence occurs only, if the initial profile is not too broad and the Ge concentration not too low, i.e., if peak concentration of the initial Ge profile is larger than 25% (at the given profile width). Otherwise, the clusters remain isolated and randomly distributed in size and space.

Comparing experiment and KLMC simulations, it is obvious that a buried nanowire could form at the V-groove bottom at the chosen Ge$^+$ ion fluence. As seen from Fig. 5, the annealing has been interrupted before all surrounding nanoclusters have disappeared, which compares to Fig. 5b).

It should be noted that the KLMC simulation uses a lattice. Thus, a wire formed by coalescence will be single crystalline, whereas an experimentally fabricated wire is expected to be polycrystalline. Therefore, the influence of grain boundaries is not taken into account in the present study.

**IV. PEARLING INSTABILITY**

For long-lasting annealing, theory predicts that a continuous wire decays. Thus, a wire is an unstable configuration. Its decay is driven by the minimization of the interfacial energy. Harmonic perturbations of the wire radius lower its interfacial energy if their wavelength is larger than the circumference of the
wire, $\lambda > 2\pi R_0$. This result has been first found by Lord Rayleigh \[1\] in 1879 for inviscid liquids. Linear stability analysis also revealed a fastest growing mode $\lambda_m$ of radius fluctuations during the initial stage of the fragmentation. Thus, perturbations with wavelength $\lambda_m$ grow at the fastest rate in time and are expected to dominate fragmentation. The value of $\lambda_m$ depends only on the specific mass-transport mechanism and not on material parameters or temperature. For liquid "wires", which changes their shape by hydrodynamic flow, a value of $\lambda_m \approx 9.02 \cdot R_0$ was predicted \[1\], which is also valid for internal volume diffusion as shown by Nichols and Mullins \[2\]. For surface diffusion, it holds

$$\lambda_m = \sqrt{22\pi R_0} \approx 8.89 \cdot R_0,$$

while for external volume diffusion the value $12.96 \cdot R_0$ was obtained for $\lambda_m$ \[2\]. With the result of the stability analysis an average droplet diameter $d_{\text{cluster}}$ can be given, if one assumes that the volume between two consecutive radii minima forms a droplet. For surface diffusion this gives

$$d_{\text{cluster}} = \sqrt[3]{6\lambda_m R_0} = 3.78 \cdot R_0.$$

In order to check the stability analysis for large amplitudes of diameter fluctuations, Monte Carlo simulations of a wire decay driven by surface diffusion were performed. Volume diffusion is explicitly prohibited within the simulation, i.e. atoms are not allowed to detach from the wire surface and vacancies can not be generated within the wire. Snap shots of the wire evolution can be seen in Fig. \[6\]. The initial wire, $R_0 = 4.3\text{ nm}$, shows after a long incubation time statistical fluctuations, which grow faster and faster with increasing amplitude. They finally lead to the disintegration of the wire after 5600 kMCS into droplets. The average diameter of these droplets is $16.4\text{ nm}$, which is in good agreement with the prediction of the linear stability analysis, $d_{\text{cluster}} = 3.78 \cdot R_0 = 16\text{ nm}$. Note that the simulation was carried out at high temperature. The ratio between the effective bond strength $E_{\text{bond}}$ and the thermal energy, $k_B T$, was set to 0.7. An absolute value of the temperature $T$ can not be given since the value of effective Ge-Ge bond strength in SiO$_2$, $E_{\text{bond}}$, is unknown. It may be estimated, however, within a good approximation from the solubility of Ge in SiO$_2$.

The stability analysis as well as the Monte Carlo simulations neglect the influence of grain boundaries of a polycrystalline wire. Grain boundary diffusion may provide another source of instability, if annealing is carried out below the melting point. Then, the size of the droplets may differ from the result given above.

V. SUMMARY

A novel fabrication method of buried nanowires by ion implantation has been demonstrated. Ge$^+$ were implanted into oxide covered Si V-grooves leading to Ge enrichment in the oxide at the V-groove bottom. There, during annealing, the Ge forms a nanowire extending along the V-groove. Other than a similar method published recently \[8\], this method should work for any implanted ion species immiscible in SiO$_2$. In particular, ion beam synthesized Au wires, which are subsequently disintegrated in regular nanocluster chains, are of interest for the fabrication of plasmonic structures \[9\].

The phase separation mechanisms were studied by means of kinetic 3D lattice Monte Carlo simulations. As shown, a cylindrical profile with Gaussian cross section may coalesce to a continuous nanowire of only a few nanometers diameter. For long-lasting thermal treatment atomistic simulations revealed the pearling
instability. A wire decays into equal-sized and equal-spaced droplets. An average droplet diameter of approximately twice the initial diameter of the wire, as it is predicted by linear stability analysis for a wire decay by interface diffusion, could be confirmed by Monte Carlo simulations.

Thus, nanocluster chains having a good periodicity over long distances can be fabricated by the fragmentation of nanowires using the pearling instability. Thereby, the droplet diameter is independent from material parameters and is controlled only by the diameter of the initial wire.

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