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Solid-state dewetting of silver-thin films: self-assembled nano-geometries

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E-mail: muhammads@ru.is**Keywords:** silver, nanostructures, solid-state dewetting, AFM, SEM

Abstract

The study presents the dynamics of solid-state dewetting of silver (Ag)-film annealed in N₂ ambient, analyzed by atomic force microscopy and scanning electron microscopy. Varying the annealing parameters (i.e. temperature and time) and Ag-film thicknesses were taken into account, to determine their effect over the solid-state dewetting of Ag-films. Several morphological evolutions from nanohole to the presence of metastable nanorings were observed. It was determined that structures annealed at high temperature (≥ 900 °C) and/or time (≥ 2 h) results in formation of metastable nanorings and whose geometrical aspects and population grew with increasing film thickness. Possible applications of the structures for fabrication of silicon nanowire arrays and photo-emitters are briefly described.

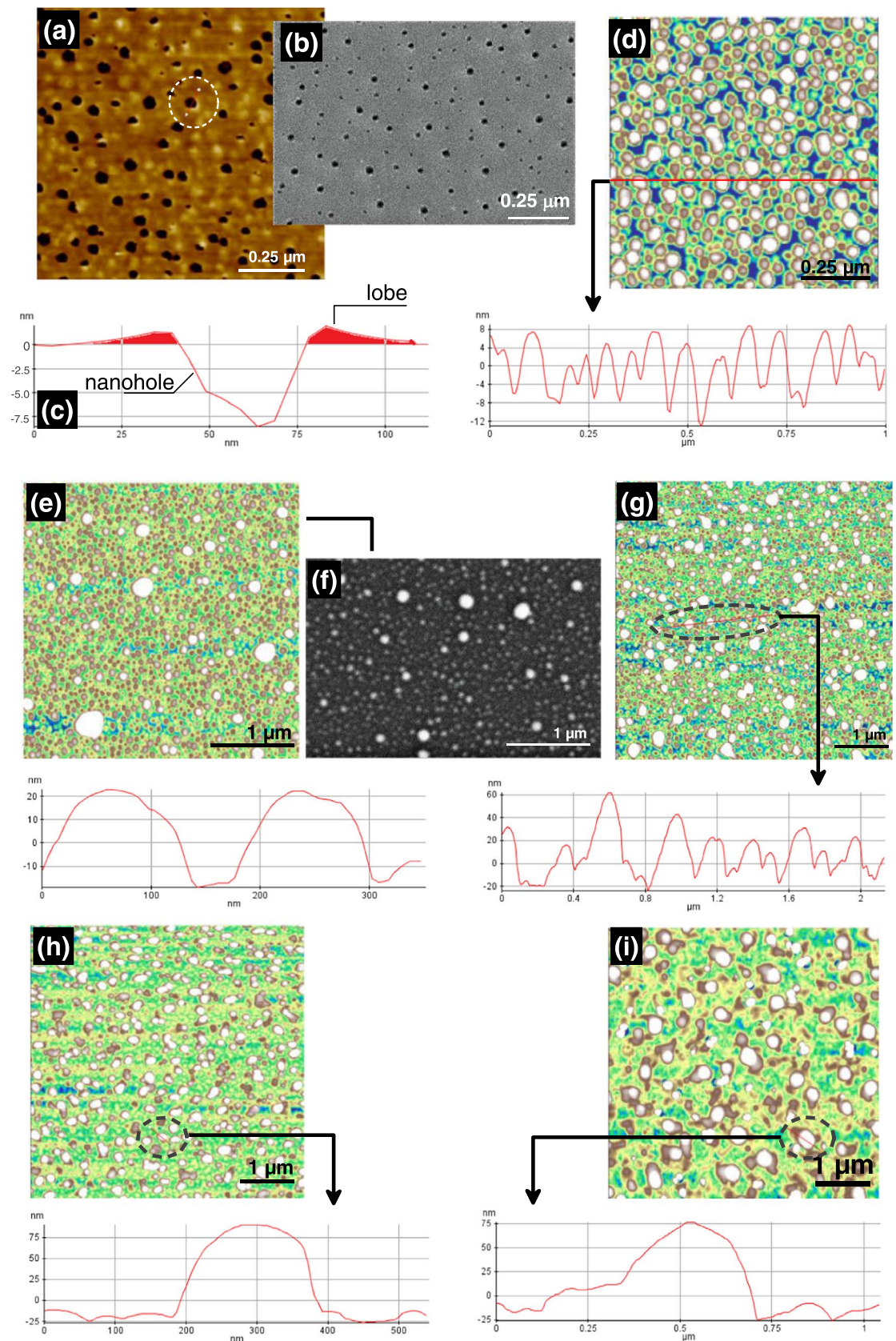
1. Introduction

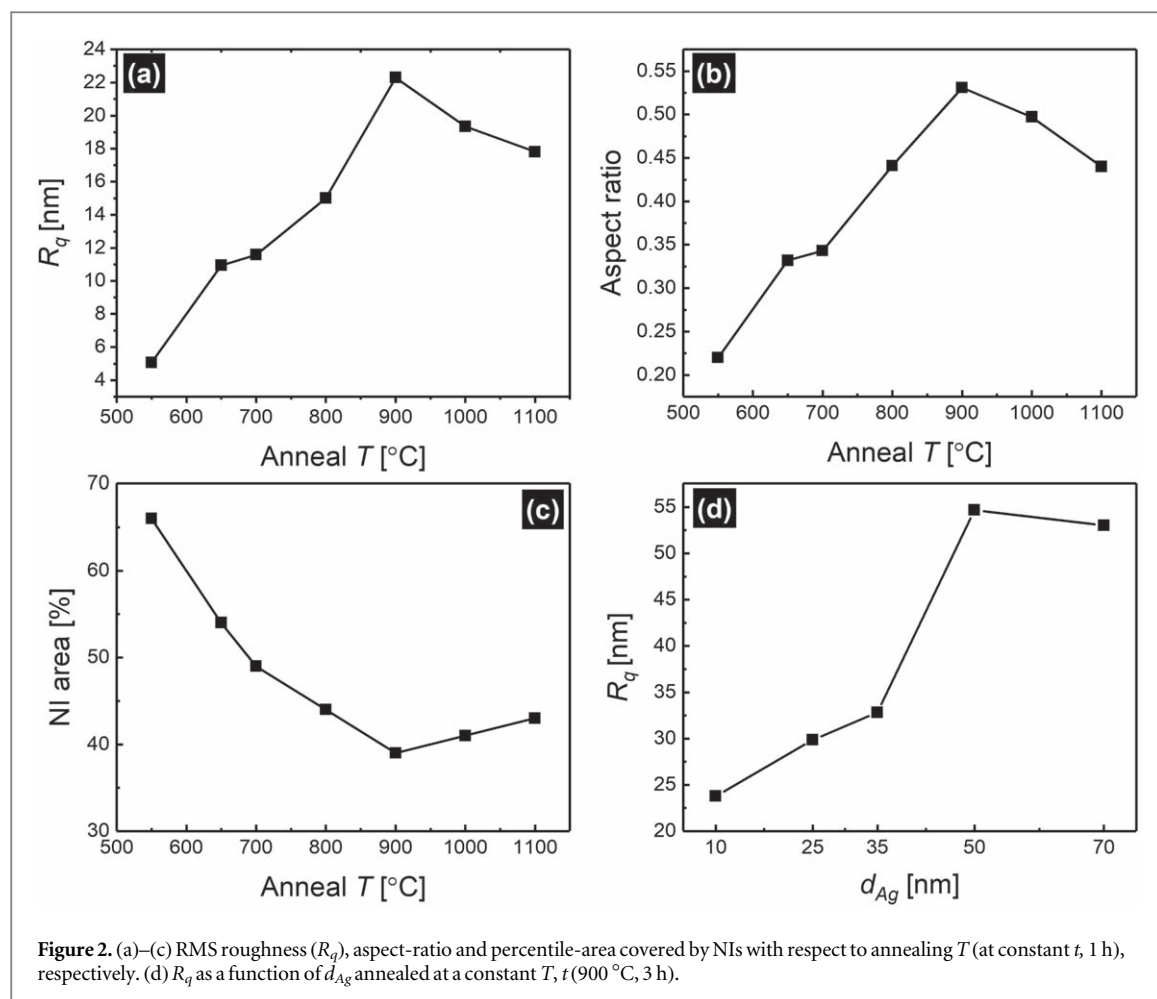
Nanostructure of silver (Ag), in the form of thin-films or having nanoscale dimensionality with various possible geometries from nanoparticles to nanowires are widely being investigated for their application in optical, optoelectronics, biomedical devices and as a metal catalyst for instance in fabrication of silicon-nanowires (SiNWs) [1–4]. Silver-nanostructures are often incorporated in devices to enhance electrical conductivity, absorption efficiency and surface plasmon resonance [1, 3].

To-date several approaches for the synthesis of Ag-nanostructures have been carried out. One relatively simple and cost effective method is to transform a noble metal-film into nanostructures with a solid-state dewetting process, offering a control over nanostructure's size, shape and density [1, 3, 5]. The driving force for the dewetting process is a reduction in total surface and interfacial energy of the system [3, 5, 6]. The dewetting of the system proceeds in the following steps: an incubation period with formation of hillocks; film pinch off, followed by hole formation, growth and percolation; later on resulting in formation and agglomeration of islands forming discrete structures as a consequence of Rayleigh instability [2, 7, 8]. The evolution of such nanostructures on oxide matrices following the above scheme can be explained on the basis of Volmer-Weber growth mode [1, 8], where the morphological modification and dewetting process is dependent on the anneal parameters and film thickness [1, 3, 5–7, 9, 10]. For further elaboration a detailed description on fabrication and material parameters, morphology of dewetted state and dewetting kinetics is given in [6, 8].

The properties of self-assembled silver nanostructures greatly depend on its morphology, including shapes, sizes, and population density. A number of efforts have been devoted to the synthesis methods and controlling the morphological development of silver nanoparticles. The present work provides a comprehensive approach, significant to the investigation of low-cost processes for the fabrication of self-assembled Ag-based nanostructure suitable for mass production. Such structure, with controllable shape and dimension on nanoscale, is promising for application in nano-devices with specific properties for instance in nanosensors, plasmon-enhanced spectroscopies, photovoltaics and as photocathodes.

In the current study, Ag-films were deposited by electron (e)-beam evaporation on single crystalline Si wafer having native oxide. The morphological transformation of dewetted Ag-films of varying thicknesses under different anneal parameters is observed with atomic force microscope (AFM) and scanning electron microscope





(SEM). Various nano-geometries obtained due to dewetting were observed i.e. nanohole and nanoislands, along with interesting self-assembled metastable nanorings due to crumpling of nanoislands when annealed at high temperatures (≥ 900 °C). A practical application of the obtained nanostructure as a metal-catalyst for fabrication of SiNWs and as a photocathode is briefly demonstrated.

2. Material and methods

A structure comprised of Ag on SiO₂/Si was prepared by e-beam evaporator (Polyteknik Cryofox Explorer 500) over a 12×12 mm² p-type Si(001) substrate. Prior to deposition, the substrates were cleaned with a mixture of acetone, methanol, and isopropanol followed by rinsing with de-ionized water and purging with N₂ gas. The Ag-film was deposited at 6×10^{-6} mbar, while the sample stage was being rotated for better uniformity of the film. The structures were then subsequently annealed *ex situ* using a Heraeus D-6450 Hanau furnace [11]. Various annealing parameters, i.e. temperature T , (ranging from 350 °C to 1100 °C), time t (ranging from 1 to 5 h) and, Ag-film thicknesses d_{Ag} (ranging from 10 to 70 nm) were considered. AFM from Park System (PSIA XE-100) and SEM (Zeiss Supra 35) were utilized for structural characterization.

3. Result and discussion

Figure 1 shows the AFM micrographs of structures annealed for 1 h at T ranging from 330 °C to 1100 °C, for Ag-film of thickness ~ 10 nm. Prior to annealing, the Ag-film is in metastable configuration that tends to equilibrate [2, 3, 9], when subjected to annealing treatment. The difference in thermal expansion coefficient between Ag and SiO₂ will induce mechanical stress resulting in increased surface and interfacial energy [2, 9]. This in turn activates the process of film dewetting as to relieve or minimize the surface-free energy. Heating the structure initially at 330 °C promotes the formation and growth of holes which is a prerequisite for dewetting, where the formation of hole is governed by surface diffusion and grain growth. AFM and SEM images in figures 1(a), (b) present the formation of nanoholes with anisotropic lobe/rim around it without any evident formation of

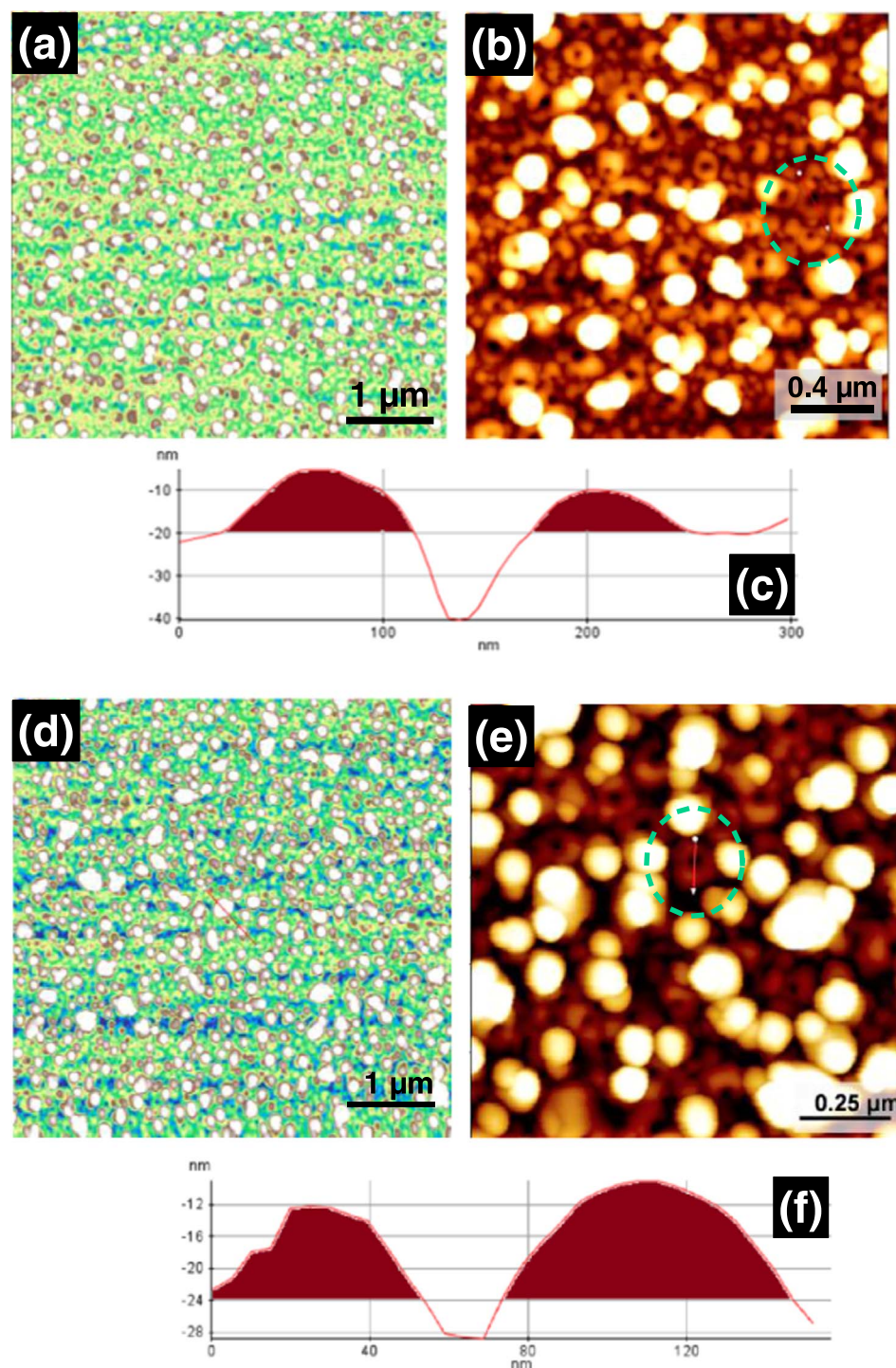


Figure 3. AFM analysis, along with corresponding line-scan over areas within the dotted circles for structure (Ag ~ 10 nm) annealed at (a)–(c) 1000 and (d)–(f) 1100 °C, respectively.

islands. A line-scan over the nanohole in figure 1(c) exhibits the hole size of an average of ~ 40 nm (width) and ~ 9 nm (depth), with anisotropic lobe around it represented by red shaded area.

With increased temperature, the surface coverage decreases (i.e. percolation of holes), after which the system becomes unstable and breaks up into stable islands as to minimize the Gibbs free energy of the system [2, 3]. To study the effect of annealing parameters Ag-film of ~ 10 nm was considered, as the formation of holes is facile for thinner films [1–3]. As depicted from AFM analysis in figures 1(d), (f), (i), (k), (m) for structures annealed at 550 °C, 650 °C, 700 °C, 800 °C and 900 °C, respectively, the resulting Ag-nanoislands gradually evolved from smaller densely compact nanoislands (NIs) to larger and mildly spaced NIs, where the solid-state dewetting is governed by the surface diffusion of thermally activated Ag-adatoms below their melting point [1]. The size of the NIs increases, and the density decrease with increased annealing T , due to coalescence, where the small NIs are being

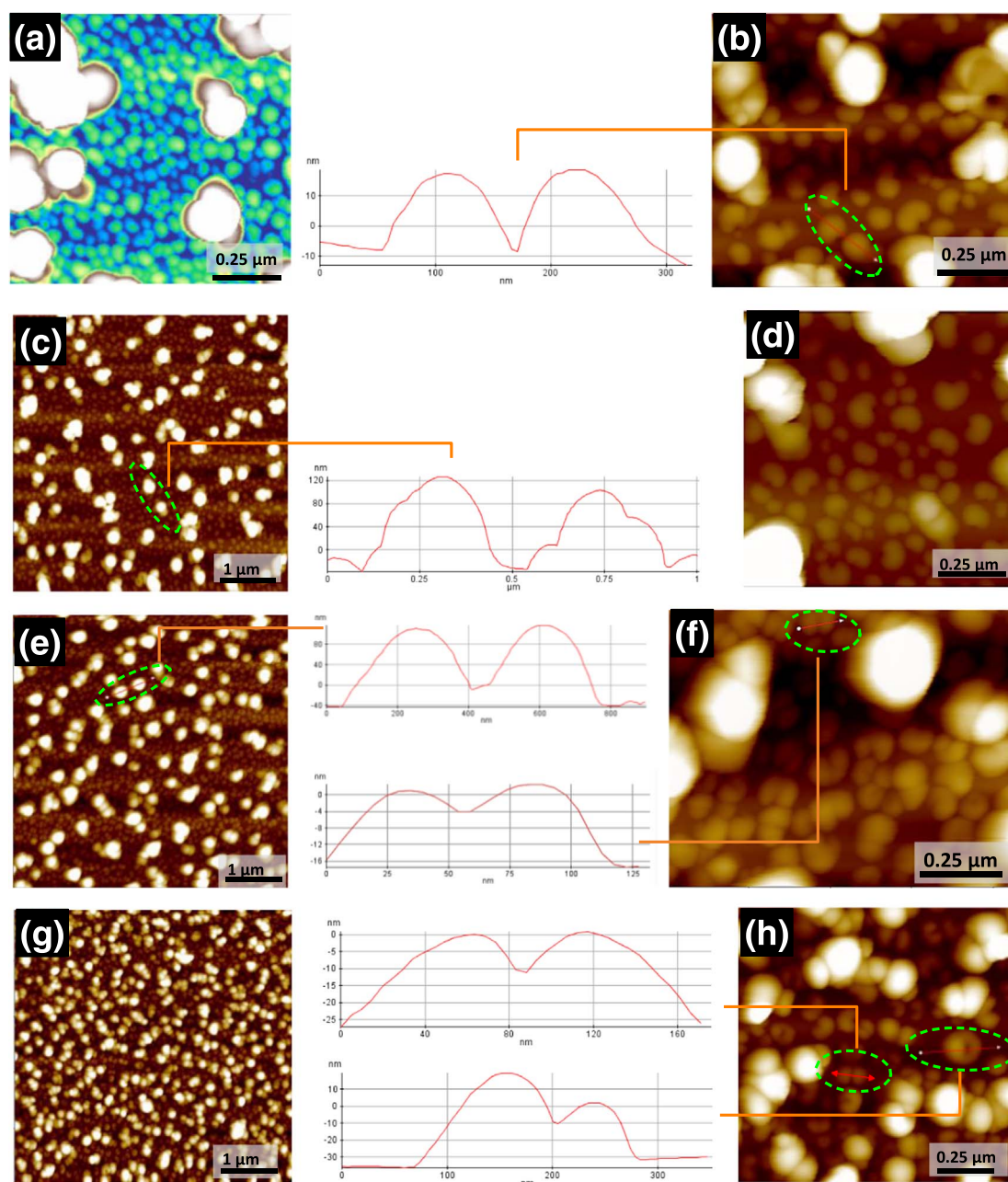


Figure 4. AFM analysis of structure ($\text{Ag} \sim 10 \text{ nm}$) annealed at 900°C for (a) 1 h, (b) 1.5 h, (c), (d) 2 h, (e), (f) 3 h and (g), (h) 5 h, respectively. The line-scans over areas within the dotted circles are incorporated for respective figures.

ripened i.e. absorbed by large ones due to difference in surface energy [1, 9]. As the NIs size keeps increasing with increasing T , the self-assembly process become more pronounced due to weak intermolecular forces i.e. Van der Waals forces between NIs, as to minimize the total surface-free energy [1]. Each AFM micrograph in figure 1 includes a line-scan in order to visualize geometrical alteration with respect to annealing T . The variation in roughness (R_q), aspect ratio and percentage-area covered by NI (determined by using ImageJ, and AFM software) are plotted as a function of annealing T in figures 2(a)–(c). A good agreement with previous studies is observed [1, 3, 12, 13].

Furthermore, upon increasing the temperature above the melting point of Al and Al-Si eutectic T , i.e. 1000°C and 1100°C , the size of the NIs increases along with an interesting formation and presence of nanorings (NRs) (see figure 3). A line-scan was carried out giving the geometrical aspect of the NRs. Further study on evolution and formation origin of these NRs is discussed in following paragraphs.

The effect of varying annealing t (at constant T of 650°C and 900°C) and d_{Ag} ($\sim 6, 10, 25, 35, 50$ and 70 nm) were carried out to explore their effect on nano-structuring of islands and specifically the evolution of NRs. An Arrhenius-type size evolution of islands were observed for structure annealed at 650°C for 1–5 h (AFM micrographs not shown here). However, for structure annealed at 900°C at varying t or by increasing d_{Ag}

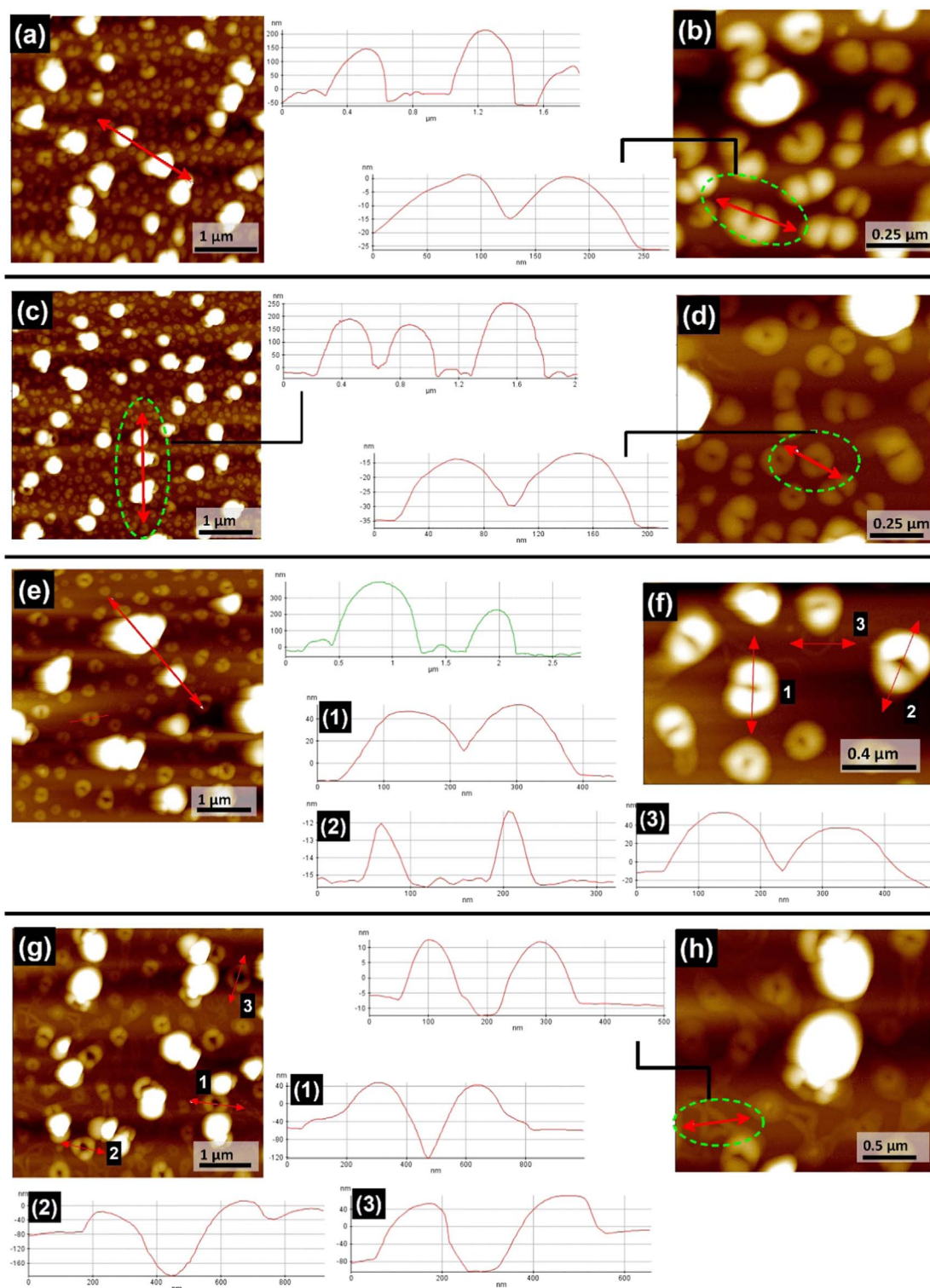


Figure 5. AFM analysis of structure annealed at 900 °C for 3 h, having d_{Ag} of ~ (a)–(b) 25 (c)–(d) 35, (e)–(f) 50 and, (g)–(h) 70 nm, respectively. The line-scans over indicated areas are incorporated for respective figures.

(annealed at 900 °C, 3 h) although the size of NIs increase, one can observe the additional presence of tiny nanoislands (figures 4(a)–(d)), which upon increased annealing T (figure 3), t (figure 4) or d_{Ag} (figures 5, 6) eventually leads to formation of NRs. AFM micrographs in figures 4 and 5 accompanies a line-scan giving a variation in size of the NIs and NRs with increasing t and d_{Ag} . It was further observed that the size of the NIs and the R_q increases with increased t and d_{Ag} , which is in good agreement with previous studies [1–3]. Additionally, the line-scan gives an estimation of variation in depth (for valleys) and heights (for walls), which has been shown to increase with increase in d_{Ag} . Various experimental and theoretical representations of formation of nanoring structures have been reported and it has been demonstrated that such NRs does exist in metastable states [14]. It

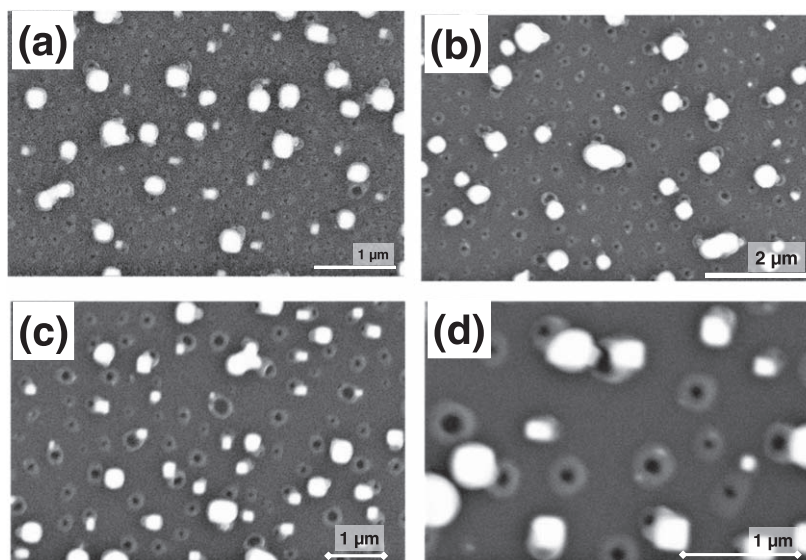


Figure 6. SEM image of structure annealed at 900 °C for 3 h, having d_{Ag} of $\sim$ (a) 35 (b) 50, and (c)–(d) 70 nm, respectively.

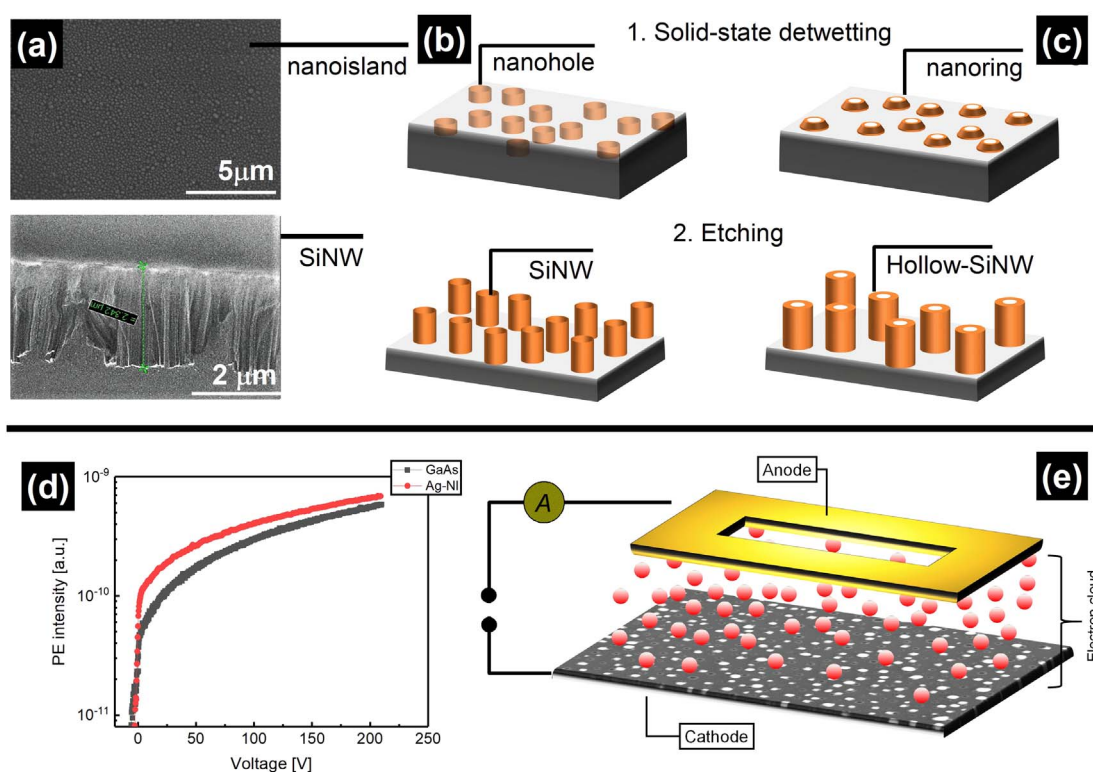


Figure 7. (a) SEM image of structure in figure 1(d) i.e. Ag film ($\sim$ 10 nm) annealed at 500 °C for 1 h (upper) and cross-sectional view of obtained SiNWs (lower) by chemical etching of the annealed structure. Schematic of SiNWs obtained by etching Ag-nanoholes (b) and (c) Ag-nanorings. (d) Comparison of PE characteristic I - V plot for GaAs and Ag-nanoislands in figures 1(d). (e) Schematic of PE setup enclosed in high-vacuum system.

has been reported that formation of such nanoring-like structures is due to buckling/crumpling of Ag-NI (i.e. formation of kink in the NIs) during high temperature annealing which results in surface corrugations and undulation as a consequence of stress-driven morphological instability. In a study by Mishra *et al* [14], the mechanism for the formation of NRs was proposed to be composed of following steps: (a) formation of islands, (b) introduction of surface corrugation, resulting in buckling of nanoislands (i.e. the initial formation of NR); (c) Ostwald ripening where the diffusional mass transport from the valleys of ring towards the wall continue with the increase in local surface curvature [6, 15] as a consequence of annealing, thus resulting in eventual formation

of NR (see SEM image in figure 6). It is noteworthy to mention here that the formation and average dimensions of self-assembled nanogeometries are reproducible for a different sample treated under similar annealing parameters. Moreover, although the formation and size of nanorings is dependent on d_{Ag} , the annealing parameters extent is limited and any further increase in T and t ($\leq 900^\circ\text{C}$ and 5 h) will tend to transform these structures into larger islands [14].

The forth coming of the present paper briefly describes implementation of size and shape-controllable Ag nanostructure as a metal catalyst for fabrication of either solid or hollow SiNWs arrays via top down approach, and as a photocathode (electron emitter) (see figure 7). Figure 7(a) presents SiNWs (with length of $\sim 3\ \mu\text{m}$) obtained from etching the structure annealed at 550°C for 1 h using $\text{HF}/\text{H}_2\text{O}_2$ etchant for 10 min Possibilities of obtaining SiNWs are schematically represented in figures 7(b)–(c). For photoemission measurement (figure 7(d)–(e)), a low-cost, low-power UV-diode ($\sim 265\ \text{nm}$, 16 mW) from Boston Electronics was utilized to illuminate Ag-nanostructured photocathode giving photoemission (PE) intensity ~ 2 -fold higher than that observed from GaAs-substrate for a bias range of -5 to $210\ \text{V}$. It was noticed that structures having nanoislands and nanorings tends to give increased PE intensity in comparison to that of structures having nanoislands only (not shown here). The above studied nanogeometries is being explored further for their potential applications in optoelectronics and photovoltaics.

4. Conclusion

In summary, formation of Ag nanostructures by annealing of Ag-film on top of flat silicon substrate was explored. It was observed that the annealing parameters and films thickness plays a vital role in determining the dewetting kinetics towards structural modifications. Evolution of various nano-geometries, including nanoholes, nanoislands and metastable nanorings, formed at different annealing parameters and various Ag-film thicknesses was demonstrated. The emergence of such nanostructures can be explained on the basis of surface diffusion, with formation of holes followed by stress-driven instability towards coalescence and islands formation to minimize the total surface-free energy of the system. High annealing parameters resulted in metastable NRs formation attributed to buckling and formation of kink in NIs. The formation of NRs was also shown to be more pronounced for larger d_{Ag} .

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary information files).

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