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Effect of surface energy anisotropy on Rayleigh-like solid-state dewetting and nanowire stability

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Abstract—Nanowires and narrow wires patterned from thin films are usually subject to a Rayleigh-like instability and, when heated, will undergo evolution to particles with a characteristic size and spacing. This process can occur while the wires remain in the solid state. For materials with isotropic surface energies, the characteristic sizes and spacings of the resulting particles or islands are expected to depend only on the initial cross-sectional area of the wires. However, crystalline solids rarely have isotropic surface energy. We show that when wires are patterned from single-crystal films, the rate of particle formation and the characteristic size and spacing of the resulting particles depend strongly on the epitaxial orientation of the film and on the in-plane orientation of the patterned wires, even for wires with the same cross-sectional areas. Wires patterned with in-plane orientations that evolve to be bound by equilibrium facets that extend along the wire axis are found to be highly resistant to dewetting. These wires very slowly dewet into widely spaced particles.

Keywords: Dewetting; Surface energy; Anisotropy; Nanowires; Rayleigh instability

1. Introduction

Nanowires and thin films evolve to form particles when heated, even at temperatures well below the material's melting temperature [1,2]. As feature sizes have decreased in evolving microsystem technologies, dewetting and beading have become increasingly problematic. This is clearly established for processes based on silicon-on-insulator structures [3–5], for silicide layers made via film–substrate reactions [6–8] and for devices used at high temperatures such as solid oxide fuel cells [9–11], and further examples are certain to emerge over time. Stability issues are of particular concern for emerging applications of free-standing nanowires, which are of interest for electronic, photonic, magnetic, sensing and other devices.

While beading and dewetting lead to constraints on fabrication and limits on the reliability of nanoscale structures and devices, there is increasing interest in the intentional use of dewetting and beading phenomena to form specific structures for various applications and devices. Dewetting of films has been used to create catalysts for nanowire [12,13] and nanotube [14,15] growth, and to make sensors and photonic devices [16–19]. For such applications, dewetting of films can be controlled through the use of topographic patterning of substrates [20,21] or by pre-patterning of the film before dewetting [22,23]. The former has been used to make arrays of particles with 2-D and 3-D order [20,21], and in some cases, crystallographic alignment [20]. The latter has been shown to be a route to reproducible formation of dewetted structures with increased complexity and smaller length scales than the pattern used to template the dewetting processes.

The late stages of dewetting of both continuous and patterned films are often dominated by the break-up of wire-like structures into arrays of particles that have regular spacings. This is also the case for nanowires made using other techniques. Break up of wire-shaped solids with high length-to-diameter ratios has been observed in various free-standing nanowires, including Cu [24], Au [1], Co [25], Ni [26], Pt [27] and Si [5], and in various composite structures, including metallic [28–31] and non-metallic [32] wire-like structures in solid matrices and Si-based [5,23,33] and metallic [34–37] wire-like patterns made on substrates. In all of these cases, the resulting particles have a characteristic spacing that scales with the initial cross-sectional area of the wire-like structure, as would be expected for a Rayleigh-like instability.

The inherent energetic instability of liquid cylinders was first discussed by Plateau [38], who observed the breakup of long cylindrical liquid jets into strings of droplets. Lord Rayleigh [39] later showed that infinite cylindrical shapes are inherently energetically unstable when perturbed at sufficiently large wavelengths, and will evolve to form arrays of drops. Later, Nichols and Mullins [40] showed that for solid cylinders with isotropic surface energies

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evolving through capillarity-driven surface diffusion, the minimum wavelength of perturbations that will grow, λ_{crit}, is $2\pi R_o$, and that the most rapidly growing wavelength $\lambda_{\max}$ is equal to $\sqrt{2}\lambda_{crit}$. Isotropic models with various other geometric bounding conditions were subsequently developed, including continuous intergranular phases [41]. McCallum et al. [42] treated the case of solid cylinders that partially wetted substrates with contact angles θ. They found that partial wetting increased the stability of wires such that, for $\lambda_{crit} = \alpha R_o$, α is higher for wetting wires (e.g. $\alpha = 8/\sqrt{3}\pi$ for $\theta = \pi/2$) than for cylinders ($\alpha = 2\pi$ for $\theta = \pi$) and that for sufficiently small θ, wires are stable with respect to all perturbations. $\lambda_{\max}/\lambda_{crit}$ was found to be approximately $\sqrt{2}$ for all metastable wetting wires (and exactly $\sqrt{2}$ for $\theta = \pi/2$ and π). In all cases, particles that form due to a Rayleigh-like instability are expected to have a characteristic spacing λ_p approximately equal to $\lambda_{\max}$, so that $\lambda_p \propto R_o$.

In single-crystal wires, an anisotropic Rayleigh-like instability is expected due to crystallographic constraints on the growth of perturbations. Cahn [43] developed a simple analytic expression for the critical perturbation wavelength of a cylindrical rod with isotropic surface energies about the axis of the cylinder, but surface energy anisotropy for planes rotated with respect to the wire axis. He showed that while the wavelength is still proportional to the initial radius of the cylinder, it also depends on the second derivative of the surface energy, which is a measure of the surface energy anisotropy. This effect can either increase or decrease the range of stability of a wire and significantly affect the spacing of particles when they form. Others have analyzed the effects of more realistic surface energy anisotropies [44–47], but at the cost of significantly increased complexity and reduced generality.

There are limited observations of the effects of surface energy anisotropy on beading of wire-like solids. Karim et al. [1] studied both polycrystalline and single-crystal Au wires and showed that the single-crystal wires had a higher scaling constant, α, than polycrystalline wires with the same diameter, suggesting that the range of

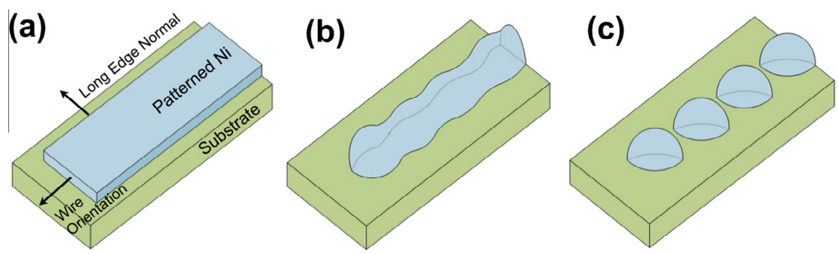

Fig. 1. Schematic illustration of the formation of a wire-like structure from a film patterned into a strip, and the subsequent development of a Rayleigh-like decomposition of the wire into an array of particles.

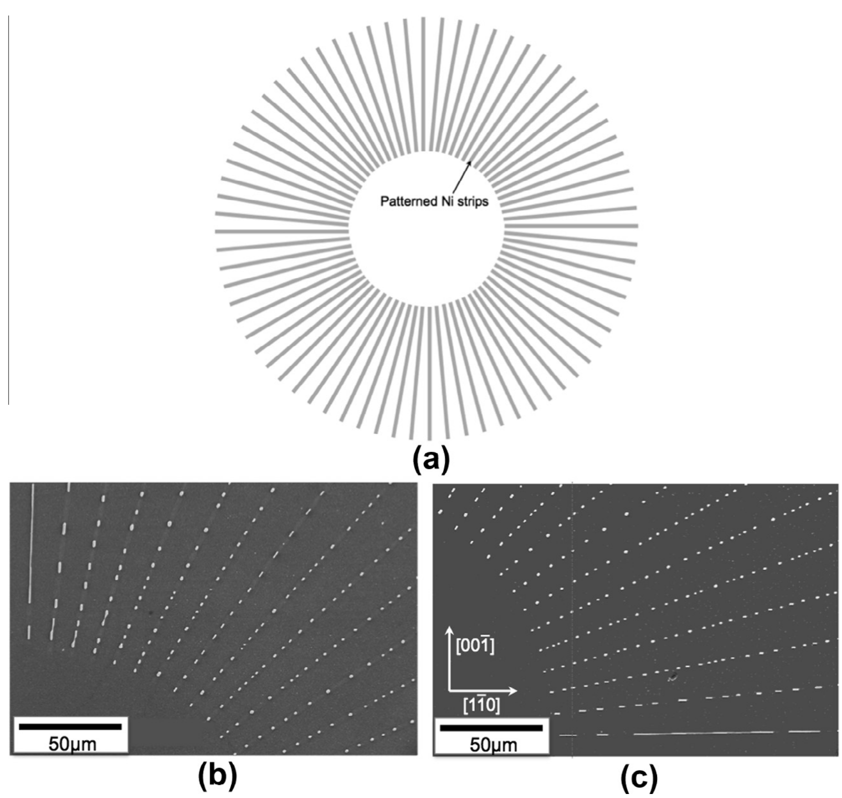

Fig. 2. (a) Schematic diagram of patterned strips. (b, c) Development of a Rayleigh-like instability in Ni(1 1 0) strips with an initial width of 2.44 μm and thickness of 0.13 μm annealed at 890 °C under 2310 sccm of reducing gas for 130 h.