Aerosol formation

Atmospheric particles from organic vapours

Aerosol particles produced over forested areas may affect climate by acting as nuclei for cloud condensation, but their composition (and hence the chemical species that drive their production) remains an open question. Here we show, to our knowledge for the first time, that these newly formed particles (3–5 nm in diameter) are composed primarily of organic species, such as cis-pinonic acid and pinic acid, produced by oxidation of terpenes in organic vapours released from the canopy.

Our technique combines aerosol electrical-mobility size measurements with organic (butanol) vapour growth rates in the cloud chamber of a modified condensation-particle counter. Particles are introduced into a condensing flow-tube cloud chamber where they are subjected to a supersaturated organic vapour. During transit through the flow tube, particles nucleate into organic cloud-droplets which are detected by light scattering on leaving the chamber.

Particles larger than 10 nm grow to the same final droplet size, whereas smaller particles grow less owing to the stronger Kelvin effect (lower effective supersaturation resulting from increased surface curvature at these sizes), resulting in a monotonic link between initial particle size and detected pulse height. In this size region, for a given size, the pulse is also dependent on particle chemical composition, owing to its solubility in the organic vapour. Therefore, if the initial size of the 3–10-nm particles is known, the composition can be determined as a function of growth in the organic vapour.

Figure 1a gives size-distribution measurements made before and during the initial stage of a nucleation event on 2 May 2000 at the Hyytiälä forest research station over the boreal forest in Finland. During the event, a clear nucleation mode (3–6 nm) is evident, together with a pre-existing particle mode at sizes over 30 nm.

Figure 1b shows the detected pulse height from droplet light scattering in the condensation-particle counter for the same event period. Before the event, the pulse height is typical of the pre-existing aerosol, with only a single distinct pulse height (and therefore droplet size) evident. During the event, additional smaller pulses are visible, corresponding to pulses generated by the 3–6-nm particles. Also shown are the calculated pulse-height responses, based on laboratory calibrations for the observed nucleation mode, which assume particle compositions of ammonium sulphate, pinic acid and cis-pinonic acid. The calculated spectra are generated by taking the laboratory pulse response for each size and composition and scaling it to the concentration measured in the corresponding mobility size range (5-nm particle laboratory pulses are shown as an example in Fig. 1b, inset).

A composition of ammonium sulphate for the measured nucleation-mode size distribution would not reproduce the observed pulse heights, but the observations agree well with those expected for pinic acid, and even better with those for cis-pinonic acid. Given that the growth of other common atmospheric aerosol inorganic species in the butanol vapour is very similar to ammonium sulphate, this nucleation mode cannot be inorganic in composition.

Although our technique does not directly demonstrate that the condensing vapour responsible for producing the new particles is cis-pinonic or pinic acid, it reveals that an organic vapour with similar solubility in butanol must be responsible for the phenomenon. Further, given that these events occur in clean air where the ratio of biogenic to anthropogenic volatile organic compounds (VOCs) is high, and the fact that biogenic VOCs are considerably more reactive than anthropogenic ones, it is unlikely that the particle production can be explained by anthropogenic species. Our results indicate that aerosol formation over forests is driven by condensable organic vapours.

Anthropogenic activities that result in increased concentrations of pollutants such as ozone will influence the conversion of natural VOCs into condensable vapours to generate natural aerosols. Complex feedback processes involving, for example, the coupling of emissions, radiative balance, and aerosol and cloud formation, possess uncertainties that must be determined if we are to predict future changes in global climate.

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Response of a strained semiconductor structure

The nanomechanical properties of thin silicon films will become increasingly critical in semiconductor devices, particularly in the context of substrates that consist of a silicon film on an insulating layer (known as silicon-on-insulator, or SOI, substrates). Here we use very small germanium nanocrystals as a new type of nanomechanical stressor to demonstrate a surprising mechanical behaviour of the thin layer of silicon in SOI substrates, and to show that there is a local reduction in the viscosity of the oxide on which the silicon layer rests. These findings have implications for the use of SOI substrates in nanoelectronic devices.

We use SOI substrates consisting of a handle wafer (a thick silicon (Si) layer), a thin oxide (about 10 nm thick) and a very thin (10 nm) template layer of crystalline Si on top of the oxide. The template layer is patterned to form micrometre-sized (5–20 μm) mesas (Fig. 1a). About 10 monolayers of germanium (Ge, total thickness 1.6 nm) are deposited by molecular-beam epitaxy at 700 °C. Germanium has a lattice constant 4% greater than that of silicon.

Figure 1b shows the formation of Ge nanocrystals (about 10 nm high, with 100-nm bases) that are crystallographically in register with the Si template, and an anomalous local bending of the Si template layer underneath each individual nanocrystal. The curvature underneath the islands is greater than 0.005 nm⁻¹. This new mode of local bending (Fig. 2a) of a nanometre-scale thin film is different from the commonly observed extended, uniform bending mode (Fig. 2b) that is induced by strained-layer film growth on thick Si (SOI) (refs 1, 2).

Our calculations show that the local bending curvature depends on the nanocrystal’s density and shape (Fig. 2c, d). On a thick substrate, local bending is suppressed, resulting in an overall extended bending that can be estimated using Stoney’s formula and which is independent of nanocrystal density and shape, as would be the case in a uniform film of equivalent thickness.

The local bending mode and large bending magnitude indicate that the Si template layer behaves as a ‘free-standing’ layer during the growth of Ge nanocrystals, an outcome that can be achieved if SiO₂ acts as a fluid with substantial viscous flow. The viscosity of SiO₂ at 700 °C (the growth temperature) is extraordinarily much too great for such a large degree of relaxation to occur. However, this viscosity can decrease almost exponentially with increasing applied shear stress.

From the bending curvature, and hence the bending stress, we estimate that the viscosity of SiO₂ can be reduced by three to five orders of magnitude in the regions beneath the bent Si layer below the Ge nanocrystals. The relaxation time for SiO₂ flow is then reduced by a few orders of magnitude, to well within the deposition time of about 150 s. Thus, the large bending stress in the Si layer greatly enhances the viscous flow of SiO₂, which in turn helps to increase the bending of the Si layer, because the Si film can then behave as a free-standing film.

The local stressor on the thin Si template layer of SOI substrate modifies both the mechanical properties of the Si layer and its electronic properties, providing a unique method for electronic (band) engineering on a nanometre scale. For these reasons, local stressors in SOI substrates could also become a significant issue for the semiconductor industry, which is increasingly using such substrates to manufacture devices.

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