

Materials science

Salting the surface

Marshall Stoneham

When one type of material is grown on a very different one, the electrostatic interactions between them become important. These interactions offer new ways to control structure on the nanoscale.

In nanotechnology, control is all-important. It is easy to produce interesting structures by chance, but much harder to build or replicate a chosen structure by design. So it makes sense to look for general principles that can guide construction even when the requirements become complex. Many of these guiding rules are extremely specialized, relying on very particular bonding behaviours or atomic geometries. So it is a step forward when a new general principle is suggested. An example appears in *Physical Review Letters*, in a recent analysis by Repp *et al.*¹ of the interface between a salt and a metal. Their work casts a new slant on electrostatic interactions between surfaces, which could provide a way of controlling structure on the nanoscale.

Most useful designs involve contact between materials that are very different in character. For example, interfaces between conductive metals and insulating ionic crystals, such as oxides and halides, are common. The oxide on metals can be helpful (as a protective oxide on aluminium beverage cans) or harmful (such as rust or corrosion products). At a smaller scale, one can use an ultrathin gate oxide on silicon in microelectronics, or metal particles on oxide substrates for catalysis. Understanding the nature of these interfaces at the nanoscale may allow greater control over the final product. With interfacial chemistry, a few general rules stem from practical experience. The most useful of these can be applied to real systems, even when such systems are too complex to be described by state-of-the-art basic science.

The most familiar of these key ideas come from crystallography, the study of crystal structures. Here, epitaxy — the geometry of fitting two crystal lattices together — is important for controlling the interface between the lattices. Then there are ideas that use macroscopic analogies with surface tension, produced when liquids wet surfaces. Another group of ideas concerns the elasticity of interfaces — for example, how a material can be deformed by structures on its surface, leading to strains that drive self-organization and restructuring.

The work of Repp *et al.*¹ emphasizes another set of ideas relating to electrostatics, in particular, the way one medium (a relatively unreactive metal) is affected by electric charges in the other (an ionic salt). We know that if a conductive material, such as copper, is in contact with an ionic material, for exam-

ple sodium chloride, the positions and charges of the ions redistribute the charge in the metal. Of course, the various interactions often influence each other. Elastic strain might interfere with epitaxy, leading to misfit dislocations, or to intermediate layers of different structure. The relative importance of the different interactions largely depends on how thick the two materials are. A very thin layer can adapt to a substrate in ways that do not work for thicker materials.

Repp and colleagues¹ have investigated the growth of a thin NaCl film on a Cu surface. Crucially, the Cu surface they have studied is not flat but has regular steps like corrugated iron. The authors used scanning tunnelling microscopy (STM) to determine the location of the sodium and chloride ions on the metal surface. The STM data show an unexpected result: the chlorine ions sit on top of the step edges, whereas the sodium ions appear to lie between the steps (Fig. 1). Such a pattern indicates a localized binding between NaCl and the underlying Cu surface. This is surprising given that Cu and NaCl are largely unreactive together.

To explain their results, Repp *et al.* revisit some old ideas involving electrostatics². The role of electrostatic interactions in metal–ionic interfaces has long been recognized³. At their simplest, ions (Na^+ , Cl^-) polarize the metal to create an attractive interaction: the ions interact with their ‘image’, or opposite, charges in the metal (so approaches like this are termed ‘image-charge models’). This model suggests that, if there is no chemical interaction, the attractive interaction might depend weakly on the

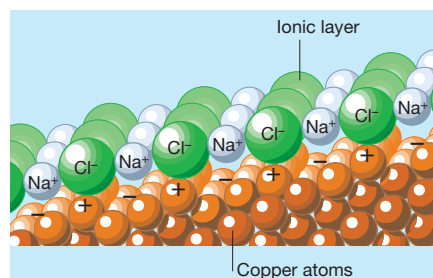


Figure 1 **Charge modulation at interfaces.** Repp *et al.*¹ observe an unusual pattern when they grow a salt (NaCl) on a stepped metal surface (Cu): the Cl ions are always located on top of the steps. This binding pattern can be explained by the Smolouchowski effect², which leads to a charge-corrugated Cu surface that forms a strong electrostatic bond especially with Cl ions.

metal, yet would depend significantly on the charges in the ionic compound. Changing the state of the ionic charges, perhaps by shining a light on the interface, could alter the interaction. The image-charge picture has become influential in studies of wetting by liquid metals, metal oxidation, catalysts supported by metals, and even, it has been suggested, in explaining how one can improve the grip of car tyres on ice with electricity.

Repp and colleagues argue that the original image-charge picture works best for very flat surfaces. But the stepped Cu surface is more complex. They note that the surface charge has an inbuilt structure in such situations (the Smolouchowski effect², first recognized in 1941). The gas of electrons inside the metal does its best to neutralize the charge of the positive ion cores. But for more complicated surfaces, with unevenly distributed surface atoms, certain ion cores are neutralized more effectively than others. On stepped and kinked surfaces, one would expect to see specific regions of positive or negative charge. When an ionic material grows on that surface, the favoured structures will have positive ions near negatively charged regions. And where the metal surface is positive, like the step edges on the Cu surface studied by Repp *et al.*, negative ions should be found, as was seen in the STM experiments.

Does this interpretation agree with earlier work? Most of the detailed theory exists for the reverse situation, where, for example, layers of metal (Ag) are grown on a metal oxide (MgO). The precise charge redistributions vary between relatively flat and more complex MgO surfaces⁴. There is no sign of the features discovered by Repp and colleagues. This may be because the ion charges are larger, swamping the Smolouchowski effect, or because the Ag layers were too thin. Certainly, other electrostatic features should be considered. Interactions between the Na and Cl ions could dominate the resulting surface structure. And more subtle effects are possible if there are additional kinks on the surface steps of NaCl⁵.

Nonetheless, the ideas of Repp *et al.*¹ suggest new ways of looking at electrostatic interactions and of explaining systematically what happens when one type of material is grown on a very different one. The idea that charge modulation can complement the more familiar ideas of crystallography, and suggest new ways to control the structures of thin films.

Marshall Stoneham is at the Centre for Materials Research, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK.

e-mail: ucapams@ucl.ac.uk

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