

rearrangement during macronucleus formation (7). These RNAs have the 5'-phosphorylated and 3'-hydroxylated termini that are characteristic of processing by Dicer-like enzymes, and so it is likely that they are members of the siRNA/miRNA family of molecules. However, they are not involved in mRNA turnover or translation arrest. A more likely role is in scanning the macronuclear genome and directing DNA deletion (7).

Intriguingly, the *Tetrahymena* RNAs implicated in macronuclear genome rearrangement are 28 nucleotides in length (7)—longer than the usual 21 nucleotides of miRNAs and siRNAs. This size difference may be significant because in *Arabidopsis* and tobacco there are also longer siRNAs/miRNAs that, like the macronuclear RNA, may influence genome rearrangements (8). These plant RNAs are up to 26 nucleotides in

length, correspond to various retroelements, and might suppress transcription or transposition of these elements. Perhaps length determines the subcellular location of short regulatory RNAs. If they are 21 nucleotides in length they could be associated with RISC, irrespective of whether they are involved in RNA cleavage. Longer RNAs may be excluded from RISC and thus available to guide other complexes that target nucleic acids in a nucleotide sequence-specific manner.

Are tiny RNAs, as suggested (1), the biological equivalent of dark matter—all around us and important but difficult to detect? The answer is almost certainly yes, although simply knowing that this “dark matter” exists does not necessarily make it easy to study, as illustrated by the difficulty of identifying miRNA targets in animals (6). Nevertheless, within

12 months of the first miRNAs report, they and similar tiny RNAs have been implicated in control of translation, RNA cleavage, and genome rearrangement. I suspect that, in due course we will find out that base pairing of miRNA/siRNA family members affects many other layers of genetic regulation.

#### References

1. G. Ruvkun, *Science* **294**, 797 (2001).
2. C. Llave, Z. Xie, K. D. Kasschau, J. C. Carrington, *Science* **297**, 2053 (2002).
3. G. Hutvagner, P. D. Zamore, *Science* **297**, 2056 (2002); published online 1 August 2002 (10.1126/science.1073827).
4. P. D. Zamore, *Science* **296**, 1265 (2002).
5. M. Tijsterman *et al.*, *Science* **295**, 694 (2002).
6. M. Rhoades *et al.*, *Cell* **110**, 513 (2002); published online 31 July 2002 (10.1016/S0092867402008632).
7. K. Mochizuki, N. A. Fine, T. Fujisawa, M. A. Gorovsky, *Cell*, 14 August 2002 (10.1016/S0092867402009091).
8. A. J. Hamilton, O. Voynet, L. Chappell, D. C. Baulcombe, *EMBO J.* **21**, 4671 (2002).
9. J. R. McConnell *et al.*, *Nature* **411**, 709 (2001).

#### PERSPECTIVES: SURFACE CHEMISTRY

## Oxidation of Metal Surfaces

H. Over and A. P. Seitsonen

Oxidation is often associated with the unwanted corrosion of materials (for example, in automobiles). But under controlled conditions, oxidation may assist the production of catalysts, semiconductor devices, or protective and functional oxide films.

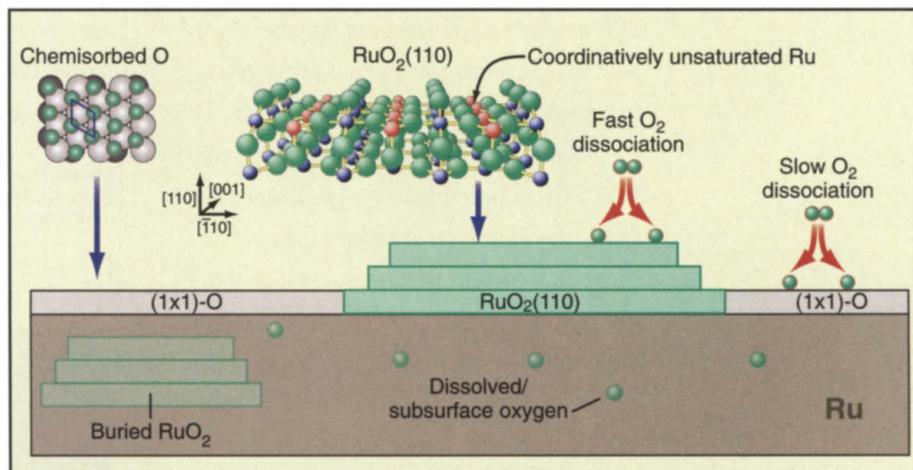
Despite this economic importance, knowledge of the atomic-scale processes behind metal oxidation remains limited (1). On page 2033 of this issue, Thürmer *et al.* (2) address this issue by investigating the oxidation of supported lead crystallites at 370 K. With time-lapse scanning tunneling microscopy, the authors show that ultrapure Pb clusters are not susceptible to corrosion when high doses of molecular oxygen from the gas phase are applied. In contrast, the presence of trace surface impurities initiates the growth of an oxide layer even at low oxygen exposures. The deliberate introduction of impurities may thus pave the way for the controlled structuring of metal surfaces by nanometerized oxide particles.

At the heart of metal oxidation is the

complex interaction of oxygen with the metal surface. The initial stage of oxidation requires a supply of atomic oxygen, together with sufficient mobility of metal atoms on the surface. Therefore, breaking the internal bonding of molecular oxygen (dissociation) on the surface represents the first elementary step in the process of corrosion. Because ultrapure Pb crystallites are chemically resistant to molecular oxygen, the dissociation of O<sub>2</sub> requires the in-

roduction of surface impurities (2), an effect that may be relevant to related metal systems. The subsequent oxide growth proceeds easily, as Pb atoms are very mobile at 370 K.

In contrast to Pb, transition metal systems readily dissociate molecular oxygen to provide atomic oxygen, which can form stable chemisorbed overlayers, the precursor to oxidation. The dissociation propensity of transition metal surfaces decreases steeply on approaching the saturation coverage of chemisorbed oxygen. Therefore, oxygen uptake beyond the saturation coverage [one monolayer in the case of Ru(0001) (3, 4) (see the figure)] becomes the rate-limiting step for oxidation. With increasing oxygen coverage, the binding energy per O atom also decreases, so that



**The rich oxygen chemistry of ruthenium (0001).** The oxidation of Ru(0001) is one of the best studied systems in the literature (10–12). Chemisorbed oxygen, surface oxide, buried oxides, and subsurface oxygen may coexist in the near-surface region. This complexity is characteristic of the oxygen chemistry of many transition metal surfaces.

H. Over is at the Physikalisch-Chemisches Institut, Universität Gießen, Heinrich-Buff-Ring 58, 35392 Gießen, Germany. E-mail: herbert.over@phys.chemie.uni-giessen.de A. P. Seitsonen is at the Physikalisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland. E-mail: ari.p.seitsonen@iki.fi

incorporation into the subsurface region may become energetically favorable.

On many surfaces, an intermediate surface oxide phase precedes the formation of the passivating oxide film, which has a typical thickness of 2 to 3 nm. Examples include oxygen on the (111) surface of silver, copper, and palladium, and the oxygen-induced missing-row reconstructions of the (110) surface of copper, nickel, and silver (5–7). Other surfaces such as Ni(001) and Al(111) oxidize directly from the chemisorbed state (8, 9).

King and co-workers (5) have argued that the critical coverage at which an oxide nucleates on an oxygen-covered surface is determined by thermodynamics: Below the critical coverage, the heat of formation of the chemisorbed phase is higher than that of the oxide. Recent ab initio calculations support this hypothesis (10). On Ru(0001), oxygen incorporation in the surface-near region sets in at a critical coverage of about one monolayer.

To investigate the oxidation process of ultrapure Pb clusters without facing kinetic limitations due to oxygen dissociation, future studies may use atomic instead of molecular oxygen. For instance, with NO<sub>2</sub> as a source for atomic oxygen, the Ru(0001) surface can accommodate large amounts (equivalent to 20 to 30 monolayers) of oxygen without surface

oxide formation, even after the oxygen-rich surface is annealed to elevated temperatures (11). This observation implies that Ru can store substantial amounts of oxygen either as subsurface (dissolved) oxygen or as buried oxide (see the figure). The presence of large amounts of dissolved oxygen is, however, difficult to reconcile with the exceedingly low solubility of oxygen in bulk ruthenium and other late transition metals. A buried oxide thus appears more likely (12).

Thürmer *et al.* (2) show that once nucleation has been initiated, the lead oxide layer grows autocatalytically in two dimensions; that is, the progressing oxidation is self-accelerated. They attribute the autocatalytic oxidation of Pb to the facile dissociation of oxygen molecules by PbO. This mechanism supplies the surface with atomic oxygen that takes part in the formation of the oxide compound.

This process of self-accelerating oxidation is not restricted to Pb. Because the sticking coefficient of oxygen increases dramatically on the oxide patches (see the figure) (4), the RuO<sub>2</sub> film on Ru(0001) grows autocatalytically in two dimensions once nucleation has been initiated (12). The further growth of thicker oxide films is generally limited by mass transport of oxygen and metal ions across the oxide film.

The work of Thürmer *et al.* (2) represents a key step toward a deeper understanding of the initial oxidation of Pb clusters and related systems. Future theoretical and experimental work should concentrate on general trends of the oxidation of metals and on their relation to physical properties of the metal systems. A comprehensive understanding of the complex atomic and molecular processes that actuate the corrosion of metals may hold technological promise for designing tailor-made materials.

#### References and Notes

1. Special issue on *Frontiers in Surface and Interface Science*, C. B. Duke, E. W. Plummer, Eds., *Surf. Sci.* **500** (2001).
2. K. Thürmer, E. Williams, J. Reutt-Robey, *Science* **297**, 2033 (2002).
3. One monolayer of oxygen is defined as the number of O atoms on the surface that is equal to the number of metal atoms in the topmost layer.
4. A. Böttcher, H. Niehus, *Phys. Rev. B* **60**, 14396 (1999).
5. C. I. Carlisle, T. Fujimoto, W. S. Sim, D. A. King, *Surf. Sci.* **470**, 15 (2000).
6. E. Lundgren *et al.*, *Phys. Rev. Lett.* **88**, 246103 (2002).
7. W. Liu, K. C. Wong, K. A. R. Mitchell, *Surf. Sci.* **339**, 151 (1995).
8. G. A. Wilhelm, A. Brodde, D. Badt, H. Wengel, H. Neddermeyer, in *The Structure of Surfaces III*, S. Y. Tong, M. A. Van Hove, X. D. Xie, Eds. (Springer, Berlin, 1991), pp. 448–455.
9. J. Trost *et al.*, *J. Chem. Phys.* **108**, 1740 (1998).
10. M. Todorova *et al.*, *Phys. Rev. Lett.* **89**, 096103 (2002).
11. Y. D. Kim, H. Over, G. Krabbes, G. Ertl, *Top. Catal.* **14**, 95 (2001).
12. H. Over *et al.*, *Surf. Sci.* **515**, 143 (2002).

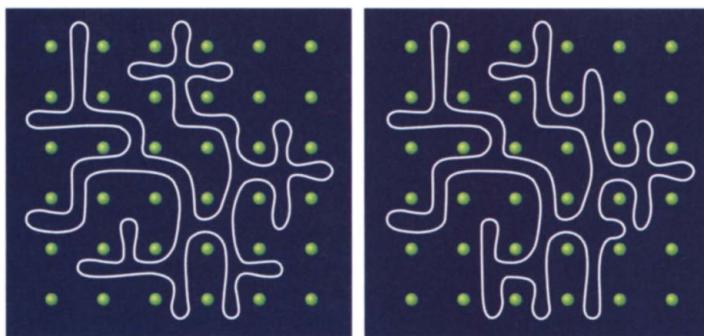
#### PERSPECTIVES: CHEMISTRY

## Polymers Without Beginning or End

Tom McLeish

“In my beginning is my end...In my end is my beginning,” reflects T. S. Eliot in his wistful *Four Quartets* (1). Ends and beginnings concern science as much as poetry, and perhaps nowhere more so than in the polymeric state of matter.

Natural polymer molecules dominate biology, while artificial polymers are used as plastics or emulsifiers in countless modern products. Many characteristics of their crystalline, glassy, and fluid states can be traced back to the special properties generated by the ends of the



**Basic dynamical move of a ring polymer entangled with a mesh of obstacles.** The obstacles arise from the presence of other loops. The whole ring moves by retraction and reconfiguration of its constituent loops.

molecules. But what would happen if there were no ends? What would be the properties of polymers composed entirely of closed loops? Answers may be within reach following the discovery reported by Bielawski *et al.* on page 2041 of this

issue (2) of a polymerization catalyst that releases the polymer in the form of a closed ring.

These are not the first ring polymers to be studied. In the 1980s, Roovers synthesized small quantities of monodisperse polystyrene rings by anionic polymerization (3). His motivation was the growing interest in the dynamics of polymer melts, in which topological entanglements between chains dominate the pattern of their motion. Experiments with linear, star-shaped, and H-shaped molecules had shown that the architecture of the molecules had a stronger influence on the viscosity and viscoelasticity than their chemistry or molecular weight. For example, the time scales for stress-relaxation in flow can increase exponentially as a function of molecular weight if the molecules are branched, but only as a power law if they are not. The promising “tube model” (4) explained these effects: The key determinant of relaxation time is the time that the locally trapped region of