

Oxide electronics

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Metal oxides have emerged as promising electronic materials of the 21st century.

Silicon occupies a preeminent position in electronics today and this unique status of Si will probably remain for many years to come. Compound semiconductors such as GaAs were considered to be good candidates to replace Si because of their versatility, but this is far from happening. Yet, one is tempted to ask the question 'Will there be a material or a class of materials as good as or superior to silicon?'. Considering the wide range of properties exhibited by them, metal oxides would appear to be the likely contenders. The nature of bonding in oxides can vary anywhere between ionic and metallic or covalent. Oxides also exhibit a phenomenal range of electronic and magnetic properties^{1,2}. Thus, we have oxides with metallic properties (e.g. RuO_2 , ReO_3 , LaNiO_3) at one end of the range and oxides with highly insulating behaviour (e.g. BaTiO_3) at the other. There are also oxides that traverse both these regimes with change in temperature, pressure or composition (e.g. V_2O_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$). Interesting electronic properties also arise from charge density waves (e.g. $\text{K}_0.3\text{MoO}_3$), charge ordering (e.g. Fe_3O_4) and defect ordering (e.g. $\text{Ca}_2\text{Mn}_2\text{O}_5$, $\text{Ca}_2\text{Fe}_2\text{O}_5$). Oxides with diverse magnetic properties anywhere from ferromagnetism (e.g. CrO_2 , SrRuO_3 , $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$) to antiferromagnetism (e.g. NiO , LaCrO_3) are known. Many oxides possess switchable orientation states as in ferroelectric (e.g. BaTiO_3 , KNbO_3) and ferroelastic (e.g. $\text{Gd}_2(\text{MoO}_4)_3$) materials. No discovery in solid-state science has created as much sensation, however, as that of high-temperature superconductivity in cuprates³. Although superconductivity in transition metal oxides has been known for some time, the highest T_c reached was around 13 K; we now have oxides with T_c 's in the region of 160 K, which is not far from the lowest temperature recorded on earth (183 K). The discovery of high- T_c cuprates has focused worldwide attention on the physics, chemistry and materials applications of metal oxides.

Many applications of oxide materials in electronics are already known. They

range from the use of oxides as insulators, capacitors, piezo-electric and pyroelectric materials, sensor materials, varistors, solid ionics, transparent conductors, and in magnetic and optical devices. In such applications, oxides are used in the form of bulk solids or thin films, generally in polycrystalline form. Fine ceramic technology is based on the control of grain size on the micrometer scale. Use of nanoparticles of oxidic materials is also gaining importance. With the progress in microelectronics, there has been much interest in the fabrication of thin films, especially in the epitaxial (high-quality single crystal) phase. A current concern in the development of large integrated silicon electronics is focused on high dielectric constant oxide films for capacitors and nonvolatile memories. In this context, heteroepitaxial growth of perovskite-type oxide films on silicon substrates is of great interest. Extensive investigations are being conducted for this purpose by employing various methods such as vacuum evaporation, sputtering, chemical vapour deposition (CVD), sol-gel process, pulsed laser deposition, and molecular beam epitaxy (MBE). Films fabricated hitherto are by no means exotic

and possess crystal structures of known perovskites, possibly with minor modifications.

The phenomenon of giant magnetoresistance (GMR), that was known earlier in metallic bilayers and magnetic semiconductors, has recently been found to occur in oxides as well. In the last year, there has been intense research on perovskite oxides of the type $\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A = alkaline earth) exhibiting GMR⁴. GMR is found in bulk oxides as well as in films and this property will clearly be exploited for several applications.

One of the highlights of advanced electronics research today relates to artificially designed structures to test device concepts based on quantum effects (quantum dots, wires and wells). For this purpose, investigations on atomic control and characterization of heterostructures are underway in many laboratories. These structures are all based on Si and related materials. Until recently, such atomically engineered oxides were not explored and were considered impossible. The situation has, however, changed since the discovery of high- T_c superconductors. The potential of oxides as advanced electronic materials has enhanced enormously because of the

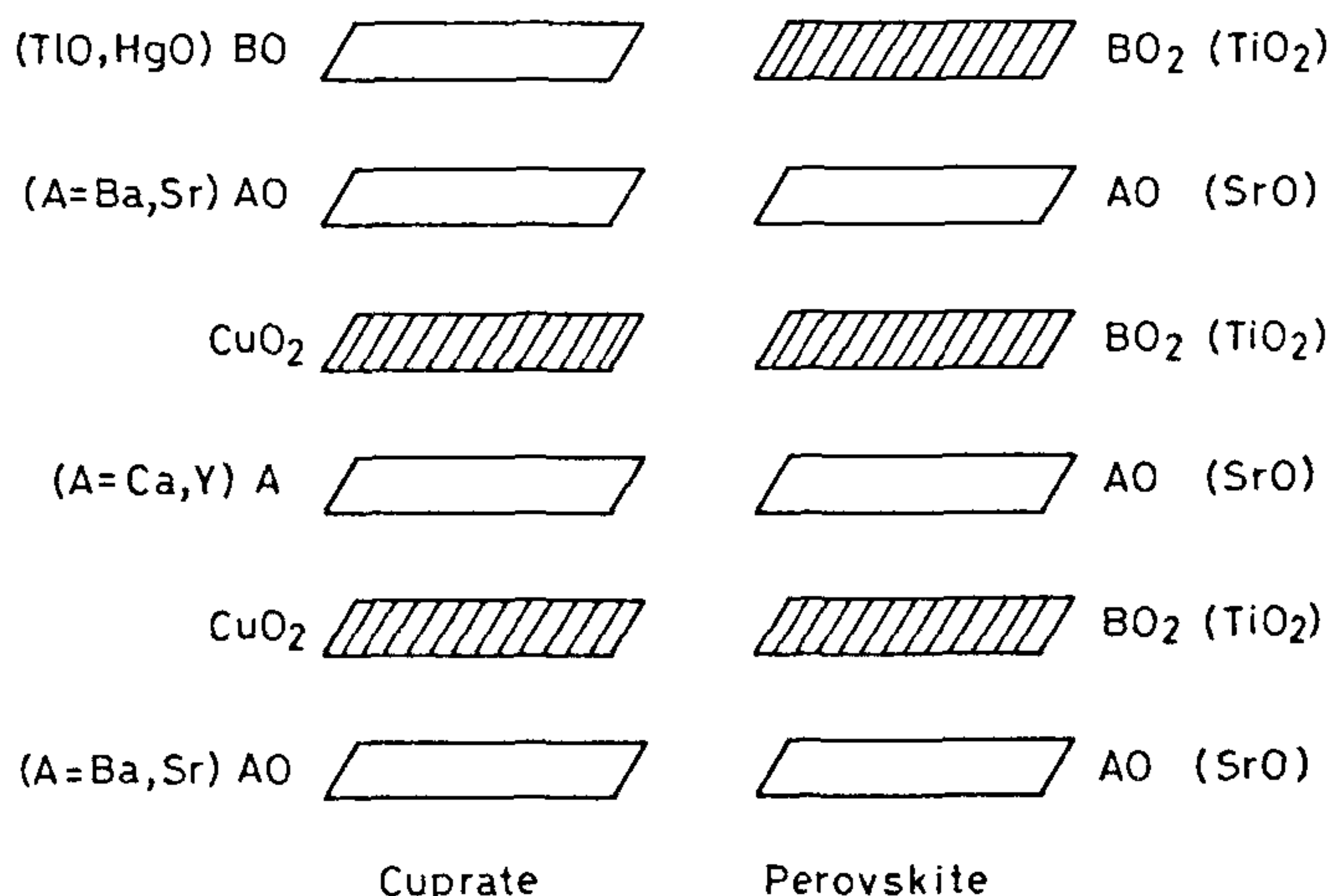


Figure 1. Layered lattice structure of perovskites and cuprate superconductors.

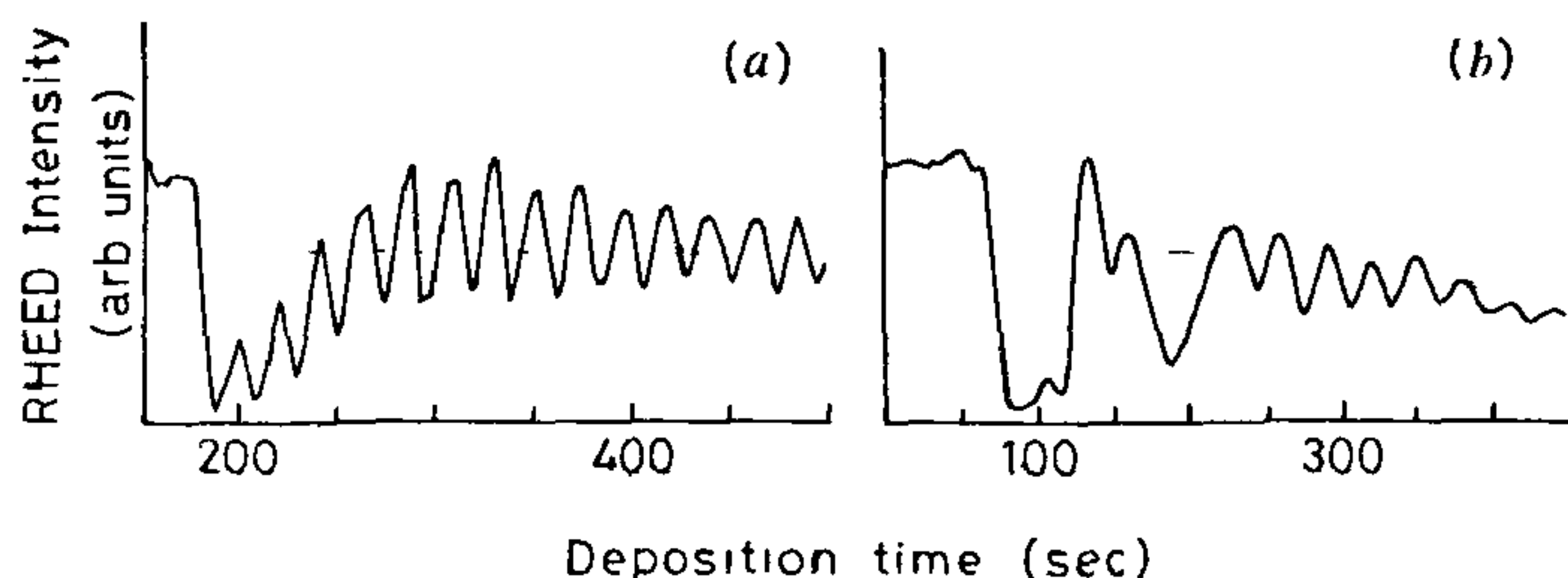


Figure 2. RHEED oscillations (0.4 nm) observed during the epitaxial growth of (a) SrTiO₃ (0 0 1) and (b) BaCuO₂ (0 0 1) on SrTiO₃ (0 0 1). Growth units are SrO/TiO₂, respectively (after Kawai *et al.*⁵).

possibility of growing novel or even unknown oxides layer by layer. It should be possible to fabricate a variety of hybrid devices and stacked unit cells or layers of perovskites which have good lattice matching with oxide substrates besides Si. For example, layered cuprate superconductors can be constructed or modified by depositing two-dimensional lattices (or layers) of different compositions chosen appropriately. In Figure 1, we show layered lattice structures related to perovskite oxides and high- T_c cuprates. The quality of such lattices is established by RHEED, RBS, STM, AFM and other techniques. A typical example of atomically controlled epitaxy of oxides is provided by BaCuO₂, which is a layered cuprate⁵. In Figure 2, RHEED oscillations obtained in the growth of such oxide layers are shown.

The wide range of properties of oxide systems certainly seems attractive compared to the Si/SiO₂ system, where the oxide can only provide it insulating characteristic. Valence control and impurity doping, readily accomplished in the case of Si, should be possible in oxides as

well. In the short term, however, it should be possible to fabricate superconductor-insulator-superconductor (SIS) tunnel junctions exhibiting clear I-V hysteresis above 77 K. Such an SIS junction would be useful in switching devices which are expected to work faster than conventional transistors. It should be noted that there has already been success in fabricating simple devices using superconducting films or grain boundary and step edge junctions^{6,7}. The use of oxides in combination with Si has also several possible applications in integrated devices. Clearly, there is much to be done in exploring oxides for electronic applications and in designing oxide superlattices with unexplored quantum functions. We have to find ways of doping, controlling valency and attaining the right carrier mobilities as well as in designing the right structures.

The importance of oxide electronics has been recognized widely in Japan, where there is considerable investment in this area. A large number of chemists, physicists and engineers are working on the various aspects of metal oxides, start-

ing from synthesis and characterization to device applications. The Japanese consider oxides as electronic materials of the 21st century. In Tokyo Institute of Technology alone, a dozen or more professors work in this area. It is highly desirable that strong interdisciplinary groups in this country are encouraged and supported to work on various aspects of oxides.

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Noncentrosymmetric monolayers from centrosymmetric molecules – A fresh approach to materials for frequency doubling

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The age we live in is often called the 'electronic age'. Some recent developments in physics, chemistry, materials science and engineering, however, indicate that a 'photonic era' is not too far in the future, when the role of electrons

in information technology will be played much more efficiently by photons. Signs of the transition can already be seen, e.g. in fibre-optic communication systems utilizing electrooptic devices; many believe that all-photonic devices will soon

appear. These devices for light transmission, processing and storage would be based on a variety of nonlinear optical (NLO) phenomena. The nonlinearity refers to the second- and higher-order terms in electric field (E) in the expres-