Perspective

Defect engineering of oxide surfaces: dream or reality?

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In this brief Perspective we analyze the present status of the field of defect engineering of oxide surfaces. In particular we discuss the tools and techniques available to generate, identify, quantify, and characterize point defects at oxide surfaces and the main areas where these centers play a role in practical applications.

1. Introduction and definitions

Defects, with their variable nature, concentration, and complex kinetic behavior, largely determine the functionality, durability, and properties of oxide-based devices [1]. This holds true for both extended and point defects. These latter are particularly difficult to identify due to their reduced dimensionality and low concentrations. Defects can exist in various charge states and can act as electrons/holes traps or recombination centers [2], thus altering the electrical, optical, magnetic, and chemical properties of a material. Even mechanical and thermal properties can be affected by the presence of defects [3]. On the side of applications, the nature and concentration of defects in oxides affect the efficiency, stability, and lifetime of a device. For instance, ion segregation to surfaces and interfaces may depend on the presence of point defects and can lead to performance degradation. Particularly relevant is the role of point defects at the surface of oxides (solid/gas or solid/liquid interface) [4,5,6] or at the junction between two materials (solid/solid interface) [7].

In this Perspective article we discuss the present status of use, creation, and characterization of defects on oxide surfaces, with particular attention to new approaches and techniques. The focus is on point defects: cation or anion vacancies, anti-site defects, impurity atoms, surface irregularities, low-coordinated atoms (corners, kinks), hydroxyl or peroxo groups, etc. Extended defects, dislocations, grain boundaries, etc. are not included in the discussion. We reiterate that the focus here is not on the emerging area of defects in two dimensional materials which has already shown to lead to very interesting chemical [see e.g. ref. 8] and physical [see e.g. ref. 9] consequences. Finally, one has also to mention that a distinction between surface and bulk defects is often difficult at the experimental level, and that many properties are determined by bulk more than by surface defects.

The article does not have the ambition to provide a comprehensive view of the field, but rather to focus on the state-of-the-art knowledge with a concise analysis of the tools available for the study and use of point defects at oxide surfaces. The aim is to establish where we are in terms of capability of identifying and counting point defects at oxide surfaces and of exploiting them in practical applications. The article is organized in three sections: (a) role and use, (b) generation, and (c) characterization of surface defects. For each section we provide a list of examples and a brief description, including a few representative references.

2. Potential use of defects at oxide surfaces

The most relevant impact of surface defects is on the chemistry, Table 1. Not surprisingly, the largest part of studies dealing with this topic refer to modifications of catalytic, photocatalytic or electrocatalytic properties of oxide materials [10,11,12,13,14,15]. As McFarland and Metiu wrote in a seminal review on this subject "it is very likely that doped oxide catalysts have been used before the concept was formulated explicitly […] It is possible that catalysis by doped oxides is as old as catalysis by oxides, but we were not aware of the fact" [16]. In recent years the interest towards controlling surface defects for chemical properties has increased and has involved defects engineering for cathode materials for fuel cells [17], properties of photocatalytic systems [11,13], electrodes in batteries and supercapacitors [18,19,20], etc.

A separate discussion should be dedicated to the exploding field of single atom catalysts (SAC). These are catalytic systems consisting of a transition metal atom bound to an oxide support either by new chemical bonds or directly replacing a lattice atom [21]. Before the introduction of the term SAC, these entities were simply classified as impurity atoms or extrinsic defects, as they possess the typical characteristics of dopants in a host material. The reader is referred to the abundant literature on this specific topic [21].

The other classical field where surface defects play a dominant role is gas sensors [22,23]. For instance, the ability of the surface to incorporate oxygen depends on the availability of oxygen-accommodating vacant lattice or interstitial defect sites [22]. But more in general, the adsorption of gas-phase molecules largely depends on the presence of active sites related to surface defects. These can also affect the electrical conductivity of the material, another essential characteristic of sensors [23].

The presence of surface defects is not always beneficial and may result in deterioration of the properties. Recently, new approaches have been proposed to passivate surface defects by adsorption of specific molecular complexes [24,25]. For instance, this is relevant to reduce perovskite defects and suppress ion movement, improving the performances [24].

Not less important from a technological point of view, are the studies of surface defects that affect conductive properties [26,27]. Here particularly relevant is the role of oxygen vacancies at the interface of materials forming the active part of memristor devices; ion diffusion processes are relevant for resistive switches and memristors [28,29]. An interesting possibility is the use of external electric fields to induce formation of oxygen vacancies with direct effects on the metal/insulator transition [30,31,32]. Finally, oxide point defects have an important role for ferroelectric domain walls nanoelectronics [33].

Table 1 – Processes related to point defects at oxide surfaces

	Brief description of role of defects	**Ref**
Chemical properties		
Thermal catalysis	- Change of surface reactivity - Charging of adsorbed species - Induce presence of radical species or sites - Doping with heteroatoms (including single-atom catalysts) - Promoting (or inhibiting) effects - Stabilize surface species (supported metal particles)	[16,10,11]
Photocatalysis	- Change optical absorption - Affect electron-hole recombination - Increase photocatalytic activity	[11,13]
Electrocatalysis	- Charging and activation of adsorbed species - Induce band bending	[14,15]
Electrodes for fuel cells, batteries, supercapacitors	- Modify ionic and electronic conductivity - Enhances oxygen reduction	[17,18,19,20]
Gas sensors	- Modulate amount of surface adsorbed species - Modify electrical conductivity	[22,23]
Defect passivation	- Passivation by adsorbed functional groups	[24,25]
Physical properties	-	
Conductivity, semiconductors	- Introduce donor levels in the gap; free electrons are produced by thermal activation - Formation of bands at high vacancy concentration - Introduce high mobility species	[26,27]
Memristors	- Ion or vacancy diffusion processes for resistive switches	[28,29]
Metal/insulator transition	- Induce sharp change in resistivity as function of temperature - Reversible transition as a function of vacancies concentration - Band gap opening	[30,31,32]
Ferroelectric domain walls	- Induce local bending in domain walls - Act as charge traps - Tune transport properties	[33]

3. Generation of surface defects

When talking of "defects engineering" one should not forget that the preferential sites where defects form in a material depend on their thermodynamic stability. For instance, while an oxygen vacancy prefers to form on the surface layer of the rutile TiO_2(110) surface, the same defect forms preferentially in sub-surface layers of the (101) surface of the anatase TiO_2 polymorph [34]. Thus, the idea of "defect engineering" cannot be disjoint from the intrinsic preference of some defects to segregate in the bulk rather than on the surface. Another aspect to consider is that methods to generate defects may result in high damage of the surface, with moderate control on the final structure, amorphization, formation of voids, etc.

Classical approaches to generate defects are based on chemical methods, some of which are summarized in Table 2. These include introduction of aliovalent atoms with consequent formation of vacancies to keep charge neutrality [35,36], oxygen desorption by thermal treatment in vacuum or in hydrogen atmosphere [12,37], chemical or electrochemical reduction [38,39], etc. Oxygen vacancies can also form as a result of chemical etching with reductive agents such as sodium borohydride and hydrazine hydrate [40]. In recent years it has become increasingly clear that oxygen vacancies may form in the course of a reaction at the periphery of supported metal particles, indicating a preferential removal of oxygen from these sites [41].

Other approaches to create defects imply irradiating the surface with UV-light [42,43] or with electrons [44,45,46], bombarding the surface with ions of variable kinetic energy [47,48,49,50], or by mechanical action with consequent rupture of chemical bonds [51,52]. These techniques lead to a variable level of control of position and number of oxygen defects at the surface. For instance, by UV-irradiation one can remove just a few O atoms from the surface or can reduce the system to the point that a two-dimensional electron gas forms, as for UV-irradiated $SrTiO_3$ [42]. Using ion bombardment or mechanical activation the surface is often highly damaged [53].

Completely different is the case of surface manipulation with STM and AFM tips, an area where substantial progress has been made in recent years [54]. For instance, using the tip of a non-contact AFM oxygen vacancies can be reversibly created on rutile TiO_2 by means of a voltage pulse [55], a process that can be simulated using accurate pair potentials [56]. These techniques are highly sensitive and site-specific but can be applied only to well defined surfaces and are relevant for model studies. Nevertheless, they provide information on the atomistic structure of defects and on their mobility that were simply unthinkable up to twenty years ago.

Table 2 – Methods and techniques to generate surface point defects

Method or technique	**Brief description**	**Ref**
Chemical methods		
Metal/non metal doping	- Generate charge unbalance; defects form to keep electroneutrality - Introduce heteroatoms at the surface (surface segregation) - Deposition of surface atomic species from impregnation/reduction	[35,36]
Vacuum thermal annealing	- Oxygen desorption and O vacancies formation	[37]
Hydrogen thermal treatment	- H_2 adsorption followed by H_2O desorption and O vacancies formation	[12]

Chemical reduction	- Molecular adsorption followed by thermal annealing with formation of O vacancies - Microwave assisted hydrothermal treatment - Electrochemical reduction	[38,39]
Chemical etching	- reductive chemical agents ($NaBH_4$)	[40]
Reaction produced defects (metal/oxide interfaces)	- Reduced O vacancy formation energy at periphery of supported metal particles - Formation of O vacancies due to O incorporation in an organic substrate (MvK mechanism of oxidation in catalysis)	[41]
Light irradiation		
UV-irradiation	- UV-induced O vacancy formation - Change in resistance and 2D electron-gas from O desorption	[42,43]
Surface damage		
Electron irradiation and electron bombardment	Selective removal of surface ions (formation of O vacancies)	[44,45,46]
Swift-ion bombardment	- Bombardment with ions with high kinetic energy - Induce damage, amorphization, defects clustering - Modulate defect formation by tuning energy of impacting ions	[47,48]
Ar^+ ion bombardment	- Bombardment with low-energy Ar^+ ions - Selective formation of O vacancies - Formation of sub-oxides in surface region	[49,50]
Mechanical activation (mechanochemistry)	- Electron release under ball milling due to vacancy formation (even in nonreducible oxides) - Solvent-free, low temperature treatment	[51,52]
Atomistic manipulation		
STM and AFM induced defects	- Atoms selectively removed or displaced by STM or AFM tip - Works for model studies only	[55,54]

4. Characterization of surface defects

Point defects are, by definition, elusive species. Since they are present in small amounts, their detection requires sophisticated and very sensible techniques (see Table 3). Of the three areas discussed in this Perspective, characterization is probably where progress has been most substantial. For instance, it has become common practice to combine a variety of techniques, each providing a specific piece of information, and to compare the results with supporting theoretical modeling, mostly based on DFT [57,58] leading to an atomistic representation of the defect and of its properties.

Impressive advances have been made in the imaging of materials with high-resolution microscopies. Aberration correction TEM [59,60] and STEM [61,62] have become standard approaches to visualize defects in the bulk or at the interface of materials. On model systems, the use of STM and AFM microscopies [63,64], sometimes in a combined mode, produce spectacular views of point defects and their surroundings. With an STM tip one can also do single-site spectroscopy, invaluable to study the spectroscopic features of an isolated defect [65].

On the non-local scale, beside the widely adopted UV-vis [66,67], photoluminescence [68,69], FT-IR [70,71,72], IRAS [73] and Raman [74,75] techniques, relevant information on the dynamics of surface defects can be obtained with photo-induced enhanced Raman spectroscopy (PIERS) [76]. Surface vibrations associated to defects can be detected using EELS [77,78] and REELS [79,80] in which the electron beam does not strike the sample but interacts with it via the long-ranged Coulomb

interaction. A novel sophisticated vibrational technique to detect defects is Surface action spectroscopy (SAS) [81]. This is based on the exposure of a surface at low-temperature and in UHV conditions to a messenger species (e.g. Ne or Ar); this species is then desorbed via absorption of IR light from a free-electron laser. The desorption rate at a given IR frequency provides specific information on surface structure and defect sites.

The role of EPR to identify paramagnetic impurities on oxide surfaces has grown since, beside the classical continuous wave EPR, high spectral resolution can be attained with pulse EPR at Q band frequency [82,83]. Recently even NMR spectra have been used to identify surface defects with high precision [84,85].

Widely used are X-ray absorption, X-ray emission [86,87,88], and photoemission (XPS, UPS) spectroscopies [87,88,89,90]. In particular, EXAFS is essential to determine the bond length and coordination number of atoms in the lattice while XANES provides invaluable information about the coordination number and oxidation state of impurity atoms.

Information on defects can also be obtained with less common techniques such as the Positron annihilation lifetime spectroscopy (PALS) [91,92] and the Metastable impact electron spectroscopy (MIES) [93,94]. This latter is particularly relevant since it is highly sensitive to surface species. The panorama is completed by diffraction and scattering techniques (X-ray [95,96] and neutron [97] diffraction, He scattering [98]).

Of particular relevance is the study of the dynamics of oxygen vacancies, a phenomenon crucial in catalysis [99], memristor devices [100], dielectric breakdown in insulating oxides [101], etc. There are various methods to follow the dynamical behavior of vacancies. PIERS allows for the evaluation of atomic V_o dynamics in metal oxide surfaces [76]. Dielectric spectroscopy is employed to probe high and low resistance states related to oxygen migration and to understand the dynamics of oxygen vacancies in memristors [100]. One can track the dynamic oxygen vacancy behavior with STEM, obtaining atomic-level quantitative information on phase transformation and oxygen diffusion [102]. Recently, specific doping by Gd ions of CeO_2 has been used to transform mobile oxygen vacancies into clustered or immobile vacancies [99], showing the possibility to control, to a certain extent, the mobility of these centers.

All these methods are complemented and supported by increasingly sophisticated quantum-chemical approaches either based on periodic [36,103] or on local cluster models [104,105]. Probably, the combined use of spectroscopic and microscopic measurements with well-defined structural models represents the most relevant advance in the field of defects engineering in recent years.

Table 3 – Characterization methods of surface defects

Method or technique	**Brief description**	**Ref**
Microscopies		
Aberration corrected high-resolution transmission electron microscopy (HRTEM)	- Atomic resolution, imaging of surfaces, including dopants and vacancies	[59,60]
Scanning transmission electron microscopy (STEM)	- Atomic resolution (with annular dark field (ADF) and annular bright field (ABF) detectors)	[61,62]
Scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS)	- Atomic resolution, vacancies and impurities - Requires a conducting planar support - Allows manipulation of defects - Not only microscopy, also spectroscopy	[65,63]
Atomic force microscopy (AFM)	- Atomic resolution, vacancies and impurities	[54,64]

	- Can be used also with insulating supports	
Spectroscopies		
UV-visible (UV-vis)	- Coordinatively unsaturated sites, trapped charges	[66,67]
Photoluminescence	- Intra-band-gap states associated with localized defects	[68,69]
Fourier transform infra-red (FT-IR), Infrared reflection absorption spectroscopy (IRAS)	- Adsorbed probe molecules (CO, CO_2, phosphines), functional groups (OH, peroxo, etc.) - Highly sensitive to local coordination	[70,71,72,73]
Raman spectroscopy	- Lattice defects - Vibrational properties of molecules adsorbed on surface defects	[74,75]
Photo-induced enhanced Raman spectroscopy (PIERS) Surface enhanced Raman spectroscopy (SERS)	- Evaluation of atomic dynamics of O vacancies in oxide surfaces - Stability of atomic defects at ambient pressure and under operando conditions	[76]
Electron energy loss spectroscopy (EELS) Reflection electron energy loss spectroscopy (REELS)	- Surface vibrations - Oxidation states of host cations - Detect localized electronic states in band gap	[77,78,79,80]
Surface action spectroscopy (SAS)	- Structural information independent of long-range order of the sample - Requires a free-electron laser	[81]
Electron paramagnetic resonance (EPR)	- Trapped electrons, transition metal impurities, paramagnetic F centers - Surface radical species - Highly sensitive to electron localization	[82,83]
Solid state Nuclear magnetic resonance (NMR)	- Magic-angle spinning NMR spectroscopy of adsorbed probe molecules - Highly sensitive to low amounts of dopants	[84,85]
X-ray absorption spectroscopy (XAS), extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), etc.	- Info on local structure, coordination, bond distances - Single atom catalysts, dopants	[86,87,88]
X-ray photoemission spectroscopy (XPS), Ultraviolet photoemission spectroscopy (UPS), Resonant photoemission	- Vacancies, interstitials, dopants - Chemical composition, oxidation state - Not very sensitive to low amounts of defects	[87,88,89,90]
Positron annihilation lifetime spectroscopy (PALS)	- Electron-positron annihilation photons allow measurement of the lifetime of positrons, providing information on defects	[91,92]
Metastable impact electron spectroscopy (MIES)	- Surface sensitive technique, uses excited helium atoms as a surface probe - Sensitive to small amounts of defects	[93,94]
Diffraction, scattering		
X-ray diffraction (XRD), Synchrotron X-ray diffraction (SXRD)	- Atomically resolved structural model for oxide surface, lattice constants - Defect induced lattice strain	[95,96]
Neutron diffraction	- Hydrogen impurities, oxygen defects, oxygen sublattice	[97]
He atom scattering	- Hydrogen on oxide surfaces	[98]
Quantum theory		
Periodic approaches (density functional theory, DFT)	- Electronic structure of vacancies and impurities - Theoretical spectroscopic properties - Defect formation energies	[36,103]
Local cluster model approaches (ab initio methods)	- High-level computational spectroscopy	[104,105]

5. Computational studies of surface defects

Computational characterization of defects on oxide surfaces has relied on methods based on density functional theory with the aim of increasing the accuracy of the approach [57, 103-107]. While DFT has had amazing success in providing insights into factors that control the nature of point defects at surfaces, it has well known limitations such as underestimation of band gaps and overestimation of electron delocalization and metallic character of systems, as summarized in Ref. 106. These limitations are particularly important for materials with *f* electrons, as the role of electron correlation becomes increasingly important and methods beyond DFT need to be invoked. A number of beyond DFT methods have thus been introduced to overcome these limitations for oxides, including DFT+U, application of a variety of hybrid functionals, a quantum many-electron approach [108] and dynamical mean field theory combined with DFT [109] with good success in describing characteristics of oxides that have long alluded researcher. The computational demand set by the beyond DFT approaches (except for DFT+U), however, still poses technical challenges in addressing inhomogeneities in the computational super cell as introduced by surfaces with point defects. The recent successful application of the multireference density matrix embedding theory to point defects on several oxides [101] is very encouraging.

6. What next?

Novel and advanced preparation, characterization, and simulation tools offer the potential to investigate defects in great detail, not only identifying their local environment, but also their temporal evolution during chemical reactions, the kinetics of formation and annealing, the electronic properties, the associated gap states, the absorption and emission characteristics, the capability to trap charges, etc. While this provides an unprecedented arsenal of approaches to generate and characterize point defects, it becomes increasingly clear that, due to their small dimensionality, defect properties are highly sensitive to the chemical surrounding. This is the essence of coordination chemistry, where the features of a transition metal atom can be modified by changing the ligands around the metal center. Impurity atoms or missing ions (vacancies can be considered as pseudo-atoms) may exhibit radically different properties depending on the specific structure. Even the smallest change of coordination, for instance by displacing the defect from a terrace to a step, can produce radically different properties. Despite the enormous progress done in the past twenty years, the precise identification of the defect structure still represents a challenge for theory and experiment.

Even more difficult is to generate defects with a specific and desired chemical environment. Here the progress has been marginal. Most of the methods used largely rely on tuning the preparation conditions to obtain a more or less defective sample or require to severely damage the surface with post-synthetic treatments in order to generate the defects. On the other hand, great advances have been made in model systems thanks to the use of scanning probe spectroscopies or microscopies.

There is growing evidence that defects at oxide surfaces can be exploited to improve a variety of properties, both chemical and physical. For the future what is needed is to improve measurement techniques for operation at high temperatures and complex environments, thereby enabling characterization under in situ conditions in which oxides are often used.

In summary, the capability to control defects at oxide surfaces, which is the basis of the defect engineering concept, has done significant progress but can be further improved. Given the importance that these species have in several applied fields, there is little doubt that this objective will be at the center of research interest in the next years.

Acknowledgements
Prof. Hajo Freund (FHI Berlin) and Prof. Elio Giamello (University of Torino) are gratefully acknowledged for critical reading of the manuscript. The work of GP was supported by the Italian Ministry of University and Research (MIUR) through the PRIN Project 20179337R7, and the grant Dipartimenti di Eccellenza - 2017 "Materials For Energy" and that of TSR by US National Science Foundation through grant CHE-1955343.

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