



MATERIALS SCIENCE RESEARCH • Volume 7

# **SURFACES AND INTERFACES OF GLASS AND CERAMICS**

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**MATERIALS SCIENCE RESEARCH**

**Volume 7**

**SURFACES AND INTERFACES OF  
GLASS AND CERAMICS**

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## Preface

Awareness of the great significance of surface constitution in understanding the behavior and performance of materials has been growing in proportion to the means which have become available for surface study. Recent years have seen important advances in analytical tools and methods; their applications to date will certainly suggest many other fruitful lines of investigation.

The Conference "Surfaces and Interfaces of Glass and Ceramics" held at the New York State College of Ceramics at Alfred University under the sponsorship of the U. S. Army Research Office, Durham, and the National Aeronautics and Space Administration, in August 1973, was tenth in the University Series in Ceramic Science, held in rotation among North Carolina State University, the University of California at Berkeley, the University of Notre Dame and Alfred University.

The chapters are arranged in order of their particular emphasis beginning with those principally concerned with analytical methods. Chapters dealing with friction and wear follow, highly topical in the present-day concern with efficient use of energy in finishing processes, on the one hand, and the avoidance of premature failure by frictional damage to moving parts on the other. Surface reactions are then considered, including the important questions of physiological interactions with ceramic candidates for prosthetic applications. Material-material interfaces and transition zones are discussed through examples which include grain boundaries in ceramics as well as interfaces among various solid, liquid and gaseous phases. Finally, surfaces generated by fracture are treated with respect to mechanisms and energetics of formation.

It is a pleasure to acknowledge the generous support of our faculty and staff colleagues in arranging the Conference, particularly to Mrs. Coral Link who acted as its secretary, and to Mrs. Jean Wassel who typed the photo-ready copy. Special thanks are due Dr. H. M. Davis and Dr. J. C. Hurt of AROD and Dr. James J. Gangler of NASA for the encouragement of their support and for helpful advice.

Alfred, N. Y.  
May, 1974

V. D. Frechette  
W. C. LaCourse  
V. L. Burdick

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## CHARACTERIZATION OF SURFACES AND INTERFACES

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The purpose of this paper\* is to develop an overview of the techniques that are currently available for the characterization of surfaces and interfaces. The approach is to concentrate upon external agents (for example, electrons) that may be brought to bear upon a given specimen and to indicate the kinds of observables that are available for measurement. The specific probes considered here are: (1) electrons, (2) ions, (3) photons, and (4) electric fields. Of the observables, three are chosen as externally observable. These are: (1) electrons, (2) ions/atoms, and (3) photons. Also included among the observables is material response, that is, changes in the specimen brought about by exposure to the probing agent. For the incident and observed electrons, ions and photons, energy ranges have been established which are characteristic of either fundamental phenomena or commercially available instrument development.

The basic presentation is designed to give a rapid summary of the generally observed phenomena associated with a given probe and an energy range associated with that probe. In general, a specific tool will monitor only one or perhaps two of the many quantities available for observation.

\*Work performed under the auspices of the U.S. Atomic Energy Commission.

There are two reasons for having an association of the types of interactions taking place. The first is that it may be possible to extend the capabilities of a given instrument to monitor other quantities of interest. The second is associated with possible adverse effects which may either affect the interpretation of the results or produce some irreversible change in the specimen under observation.

The table summarizes the incident probes, the observables, and the characteristic phenomena; where there are commercially available instruments that measure a specific observable, these instruments are shown in parentheses. Even in cases where an instrument is shown, not all aspects of the associated specific phenomena may be measured by the instrument noted. Electrical fields have been included as a probe purely for the sake of completeness; in general, this probing method cannot be considered to be a general purpose tool, but rather is associated with in situ study of some surface property.

## BASIC PROCESSES

### Classes of Information

There are four general classes of information<sup>1</sup> that one may seek using the interactions noted in the table.

Composition. It is frequently desirable to know the chemical composition at the surface of the specimen. In addition, knowledge of the variation in composition as one probes to greater depths of the specimen may be necessary to isolate purely surface<sup>2</sup> effects from near-surface bulk composition variations.

Structure. Given the chemical composition, it next becomes necessary to establish the surface topography, surface discontinuities which may be associated with grain boundaries, or impurity clusters. Again, this must be contrasted with bulk microscopic or macroscopic structure.

TABLE I.

OBSERVED INCIDENT	ELECTRONS		IONS/ATOMS		PHOTONS		MATERIAL RESPONSE
	0 - 5 keV	5 keV - 100 keV	0 - 20 keV	20 keV - 2 MeV	0 - 5 keV	5 keV - 100 keV	
ELECTRONS 0 - 5 keV	1. Characteristic (Auger) 2. Secondary (SEM) 3. Scattered (LEED)	X	1. Desorbed atoms 2. Ionized atoms	X	1. Optical fluorescence (microprobe) 2. X-ray fluorescence (Appearance potential spectroscopy)	X	1. Broken chemical bonds 2. Compositional changes on surface 3. Color center formation 4. Thermal effects 5. Surface charging
5 keV - 100 keV	1. Characteristic (Auger) 2. Secondary (SEM) 3. Scattered (RHEED) (SEM)	1. Characteristic (Auger) 2. Secondary (SEM) 3. Scattered (RHEED)	1. Desorbed atoms 2. Ionized atoms	X	1. Optical fluorescence (microprobe) 2. X-ray fluorescence (microprobe)	1. X-ray fluorescence (microprobe)	
IONS 0 - 20 keV	1. Secondary 2. Characteristic (Auger)	X	1. Scattered (LEBS) 2. Secondary ions (SIS) 3. Sputtering 4. Implantation 5. Desorbed atoms	X	1. Optical fluorescence 2. X-ray fluorescence	X	1. Atom displacement (radiation damage) 2. Broken chemical bonds 3. Color center formation 4. Stress/strain field formation 5. Thermal effects near surface 6. Surface charging 7. Compositional change at surface
20 keV - 2 MeV	1. Secondary 2. Characteristic (Auger)	1. Secondary 2. Characteristic	1. Secondary ions 2. Sputtering 3. Implantation	1. Scattered (HEBS) 2. Secondary ions 3. Implantation	1. Optical fluorescence 2. X-ray fluorescence	1. Optical fluorescence 2. X-ray fluorescence 3. Nuclear gammas	
PHOTONS 0 - 5 keV	1. Photo electrons (ESCA) 2. Characteristic (Auger)	X	1. Desorbed atoms 2. Ionized atoms	X	1. Optical fluorescence 2. X-ray fluorescence 3. Reflected photons 4. Scattered photons	X	1. Color center formation 2. Broken chemical bonds 3. Composition changes near surface.
5 keV - 100 keV	1. Photo electrons 2. Secondary 3. Characteristic (Auger)	1. Photo electrons 2. Secondary 3. Characteristic (Auger)	1. Desorbed atoms 2. Ionized atoms	1. Ionized atoms	1. Optical fluorescence 2. X-ray fluorescence 3. Scattered photons	1. X-ray fluorescence 2. Scattered photons	
ELECTRIC FIELDS	1. Electron emission from surface (FEM) 2. Spark generation in high stress gradient situations.	X	1. Ion emission from surface (FIM)	X	1. Optical fluorescence	X	

Chemical State. For chemical interactions between the specimen and the outside world it is extremely desirable to know the chemical binding state of the atoms at the surface, again as contrasted with the bulk.

Electronic State. For special kinds of interactions, the distribution of electrons between valence states, impurity levels, and the conduction band may greatly influence the nature of the chemical or physical interactions at the surface of the specimen.

### Interactions

In attempting to generate an overview of useful techniques for characterizing surfaces and interfaces, it is necessary to realize that the incident probe and the observable associated with that probe are connected generally by a complex sequence of events. By appreciating the basic nature of these events, it is possible to develop an intuitive feeling for the techniques that are capable of being applied in a quantitative manner as opposed to those that are inherently qualitative.

Dominant Interactions. Within the various combinations of probes and observables, it is possible to identify those where the dominant interaction is basically binary in nature. An example is the ionization of an atom by an electron resulting in the emission of an x-ray. In other interactions, more complex in nature, a collective response on the part of the atoms in the specimen give rise to the observable. An example of this class of interaction would be the emission of low energy secondary electrons resulting from exposure of the sample to the beam of a scanning electron microscope.

<u>Binary</u>	<u>Collective</u>
Auger Electron Production	Electron Diffraction
X-ray Production	Secondary Electron Emission
Ion Scattering	Secondary Ion Emission
Photo-Electron Production	Desorption of Ions or Atoms

Nuclear Gamma Ray Pro- duction	Sputtering Process Optical Photon Production Optical Photon Reflection
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### General Characteristics of Probes

Electrons. Electron beams are potentially the most useful general tool for material characterization. One reason is that electron beams having energies above several keV may be focused to dimensions smaller than typical grain sizes. At higher energies, beams may be focused to dimensions of the order of 10 nm or less. The dominant interactions of beam electrons are with the bound electrons within the specimen. Binary events can, in principle, be quantitatively predicted. Collective interactions can result in a wide variety of scattered primary electrons and secondary electrons. The scattered primary electrons that satisfy the conditions for constructive interference can give much useful information regarding short- and long-range order. In addition, these primary electrons may break chemical bonds, deposit a large amount of thermal energy on the surface of the specimen, and by charge collection on the surface of the specimen, produce very high surface potentials.

Ions. The dominant interaction associated with energetic incident ions is momentum transfer to the specimen atoms. This can result in sputtering, secondary ion production, and scattered primary ions. For high energy ions of lower mass, ionization and excitation of atomic electron shells may take place. The diameter of ion beams is generally larger than one micrometer and is frequently on the order of millimeters. Only in a few demonstrated practical cases have ion probe techniques been used to obtain surface structural information. The detrimental effects associated with ion beams are generally direct consequences of atom displacement. These displacements may result in breaking chemical bonds, production of thermal spikes, general heating near the surface, and charging of the surface to high potentials.



Photons. Photons include optical photons, through high energy x-rays. Depending upon the energy and wavelength of the photons, and the density of free and bound electrons at the surface of a specimen, many qualitatively different phenomena take place. The dominant interactions of photons of energy less than 100 keV are with electrons.

Many optical techniques are being employed for the analysis of surfaces. This general field will not be reviewed here. IR spectroscopic techniques have proved to be of great value in the analysis of chemical bonds. One specific technique has evolved in the recent years due to the ready availability of high-speed computers. This technique is referred to as ellipsometry and requires complex calculations to reduce the data to the fundamental quantities of interest - namely, the real and imaginary indices of refraction at the surface.

With photons of higher energy, absorption processes start to dominate. This results in absorption of the photons in the near-surface region. When absorption is associated with the ejection of electrons from atomic levels, two characteristic processes result. Observation of the photoelectron is employed in Electron Spectrometry for Chemical Analysis (ESCA). When characteristic electrons result from the radiationless reorganization of the atom, the Auger Electron Spectrometry (AES) technique is invoked. In view of the basic interaction of photons with electrons, effects associated with the breaking of chemical bonds may be expected. One effect may be change of composition of the specimen near the surface.

## CURRENT TECHNIQUES AND METHODS

The system characteristics of a practical instrument reflect the characteristics of both the exciting agency and the system for detecting the observable. In general, the major improvements have been associated with greater sophistication in detection and with expansion of the num-