

Probing the initial stages of solid state reactions

Sonia Pin

Dipartimento di Chimica Fisica “M. Rolla”, Università di Pavia, Viale Taramelli 16, 27100 Pavia, Italy
Université Joseph Fourier de Grenoble - LEPMI (UMR, CNRS, INPG, UJF N°5631)
sonia.pin@unipv.it

Solid state reactions are of extreme interest both for technological applications and from the point of view of basic science. For example almost all ceramics materials are currently prepared by solid state synthesis. On the other side, reactions in the solid state occur in many geological processes such as mineral metamorphism.

The kinetics and mechanisms of these reactions are normally studied making use of mono-dimensional chemical diffusion experiments. In these experiments two single crystals (or well-sintered pellets) of the reacting solids are kept in contact at high temperature and the thickness of the product layer that forms in between is measured as a function of time. When the layer thickness exceeds a certain value (usually $> 1 \mu\text{m}$) the growth of the product layer is fully controlled by the diffusion of some constituents inside the product layer itself. The theory underlying these experiments ([1]) assumes that local chemical equilibrium is attained in this regime at both interfaces (between each reagent phase and the product phase), and shows that the layer thickness increases with the square root of time, according to a parabolic growth law. The excellent agreement between the measured rate constant and independently obtained diffusion coefficient data then gives a trustworthy assessment of the reaction mechanism in the long reaction time regime.

However, very little is known about the very early stages of this kind of processes, when local chemical equilibrium is not yet obtained at the interfaces and the chemical kinetics is not driven by long range diffusion. In particular the mechanisms and the kinetics of the interfacial reactions which represent the ‘true’ chemical reactions are completely unknown.

This is largely due to the lack of both an experimental probe and an established procedure for studying such aspects. As a matter of fact, in a quite recent paper by our group it has been demonstrated that some insight into the mechanisms and the kinetics of solid state reactions can be obtained by: i) performing the reaction using at least one of the reactant in form of a very thin film (of the order of 10 nm), ii) using a local probe for the local chemical environment of one of the constituents such as XAFS (X-Ray Absorption Fine Structure) [2].

In the previous work, the reaction $\text{NiO} + \text{Al}_2\text{O}_3 \rightarrow \text{NiAl}_2\text{O}_4$ has been studied. Aim of this thesis is the study of the reactivity in the early stages, using the reaction between ZnO and $\alpha\text{-Al}_2\text{O}_3$ as a model. This system has been chosen as: i) ZnAl_2O_4 is a normal spinel [3], ii) in the ZnO/ Al_2O_3 system, the oxygen framework has to rearrange from a hexagonal-close-packed (hcp) to a face-centered-cubic (fcc) arrangement at both reaction fronts: on the contrary in the NiO/ Al_2O_3 system, the rearrangement of the oxygen framework occurs only at a single interface (spinel/sapphire).

A quite large number of topotactical relationship can be found for the interfaces between ZnO and Al_2O_3 [4], but no systematic studies have been reported up to now. In particular no studies have been performed in the early stages. For this reason, during the PhD period, we performed a strategy for studying the early stages by means of a specific model and a synergic use of several techniques.

The proposed method is divided into different steps:

1) Thin film deposition

ZnO films have been deposited at room temperature [5] by RF-magnetron sputtering of ZnO powders (Aldrich, 99.99 %) onto Al_2O_3 single crystals having three different orientations, *i.e.* (0001), (11-20) and (1-102) (MaTecK). After the deposition the films have been treated at different temperature for different

Table 1: Heating treatments for the three studied interfaces.

Temperature	Heating Time
300 °C	20 minutes
600 °C	20 minutes
800 °C	20 minutes
800 °C	40 minutes
800 °C	60 minutes
800 °C	120 minutes

amounts of time, as reported in Tab. 1. The film thickness was estimated to be ~ 15 nm by means of the Debye-Sherrer equation.

All the treatments have been done in air. After each of the treatment one film for each interface has been picked up from the batch.

2) Study of the surface morphology

AFM images of the deposited and reacted interfaces were collected with an Autoprobe CP Research scanning probe microscopy (SPM, VEECO), operating in contact mode, by means of sharpened pyramidal silicon tips (curvature radius < 20 nm) onto V-shaped cantilevers (resonant frequency, 120 kHz; force constant, 0.5 N/m). For each analysed sample, scans of different areas were carried out with a resolution of 512 pixels and a scan rate ranging between 1.0 and 1.5 Hz. A standard second-order flattening processing of the images was performed in order to correct the scanner non linearity.

We observed different reactivity for different substrates and in particular for two orientation the formation of nanocrystals on the surface of the reactive interface.

3) Fluorescence EXAFS measurements

Fluorescence XAFS (X-ray Absorption Fine Structure) data at the Zn-K edge were collected at GILDA beamline [6] of the European Synchrotron Radiation Facility (ESRF, Grenoble). A Si(3 1 1) double crystal monochromator was used; the harmonic rejection was realised by Pd mirrors, having a cut-off energy of 20 keV. A 13-elements High Purity Germanium detector was used for the collection of the fluorescence spectra, with the samples at 14.5° (84.5°) with respect to the incoming beam, that is with the radiation electric field nearly parallel (perpendicular) to the sample surface, PAR (PER) orientation. The measurements were performed at room temperature. To obtain a reasonable signal to noise ratio, the integration time was adjusted to give $\sim 10^6$ counts in the fluorescence channel. In addition, in order to avoid distortions of the spectra, the count rate of each element was kept well below the saturation limit. For the XANES (X-ray Absorption Near Edge Structure) analysis the spectra were processed by subtracting the smooth pre-edge background fitted with a straight line. Each spectrum was then normalized to unit absorption at 800 eV above the edge, where the EXAFS (Extended X-ray Absorption Fine Structure) oscillations were not visible any more.

Figure 1 shows, as an example, the raw fluorescence data at the Zn-K edge for the ZnO film onto Al_2O_3 (11-20) after a thermal treatment at 300 °C for 20 minutes: for this spectrum the electrical field vector is perpendicular to the sample surface.

The statistical noise was estimated by fitting the spectrum after 10400 eV, *i.e.* where the EXAFS oscillations are no longer visible, with a straight line. After normalization for the edge jump the noise was estimated to be 10^{-3} : this figure is representative of the quality of all the collected spectra. Given that the samples are challenging, this value for the noise should be regarded as very good.

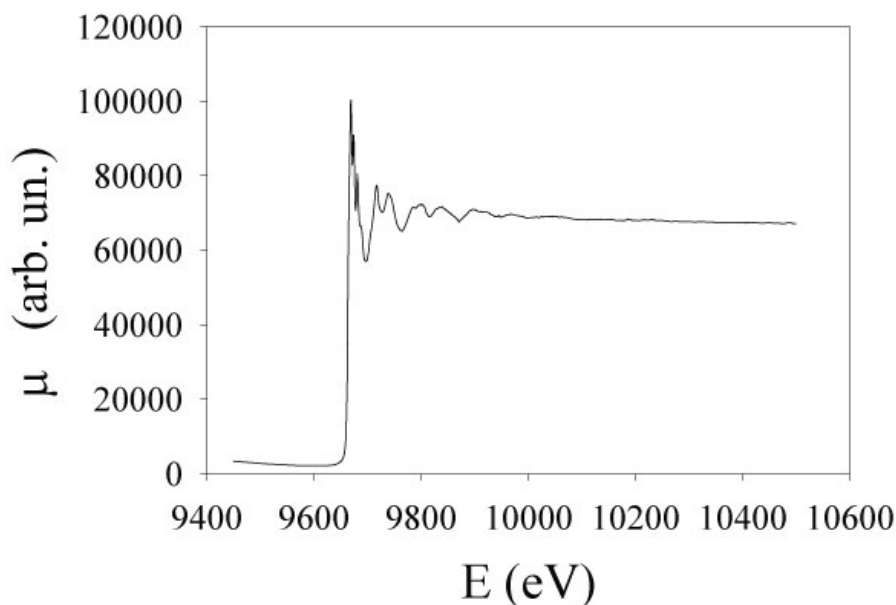


Fig. 1: Example of collected fluorescence-EXAFS at Zn-K edge for the interface ZnO||Al₂O₃ (11-20).

The EXAFS fitting has been performed by means of the FEFF8 code [6]. The goodness of fit (GOF) parameter which is scaled to the magnitude of the data itself is defined as:

$$R = \frac{\sum_{i=1}^N \{ [Re(f_i)]^2 + [Im(f_i)]^2 \}}{\sum_{i=1}^N \{ [Re(\chi_{data})]^2 + [Im(\chi_{data})]^2 \}}$$

This number gives a sum-of-squares measurement of the fractional misfit. For good fits to carefully measured data on concentrated samples, $R \geq 0.02$. The accuracy of amplitude and phase-calculated by the program have been checked by fitting the spectrum of powdered ZnO, and comparing the fitted radial distances with crystallographic values, that have been recovered with an accuracy better than 0.01 Å.

A second parameter useful to control the GOF is the so called Bond Valence Sum (BVS) [7], that is a popular method in coordination chemistry to estimate the oxidation state of the atoms. The basic idea is that the valence V of an atom is the sum of the individual bond valences v_i surrounding the atom:

$$V = \sum (v_i)$$

The individual bond valences in turn are calculated from the observed bond lengths.

$$v_i = e^{\left(\frac{R_0 - R_i}{b}\right)}$$

Where R_i is the length obtained by the fitting procedure, R_0 is tabulated and b is a constant, typically 0.37.

4) X-Ray Powder Diffraction and Surface Diffraction

X-Ray Powder Diffraction (XRPD) patterns have been collected in Pavia with a D8 Brucker powder diffractometer equipped with a Cu anticathode, an incident slit of 0.5°, an antiscatter slit of 0.5°, a detector slit of 1 mm, and a graphite monochromator on the diffracted beam, using an angular step of 0.02° (2θ) and a count time of 35 seconds per point; Surface X-Ray Diffraction (SXRD) have been collected at the

ID03 beamline at the ESRF. The sample was mounted on the z-axis diffractometer of ID03 (EH1) and surface diffraction patterns have been acquired. We have been able to obtain diffraction effects from the nanocrystals on the sapphire surface.

5) Micro-XANES measurements

After a particular polishing operation to expose the reacted interface, the samples have been analyzed at the ID24 beamline at the ESRF. They have been mounted with the surface perpendicular to the incoming beam. A silicon diode detector, mounted close to the sample at an angle of 45 ° degrees, was used to collect the Zn-K edge XANES spectra in fluorescence mode. The beam was focused with a horizontal (vertical) FWHM of 7 (150) μm . Zn-K edge spectra have been then acquired across the sample, after calibration in energy by the acquisition of a spectrum of a Zn foil. With this experiment we have used the microXANES spectra to construct a sort of map of the buried interfaces, by collecting a series of spectra along one direction of the surface of the polished sample. Owing to our sample preparation procedure, a nano-metric resolution has been obtained even with a probe with micrometric dimension. In addition, with this kind of approach, the possibility of having both compositional and structural information about a buried interface in one shot has been established as possible.

6) TEM Measurements

Preliminary Transmission Electron Microscopy (TEM) investigations were performed on the samples using an FEI Tecnai F20 apparatus operating at 200 kV. The specimens were cooled by a temperature controlled LN holder. Scanning transmission electron microscopy (STEM) images were recorded using a high angle dark field detector.

The present long abstract briefly described the use of a model and a possible experimental strategy for the study of the early stages of solid state reactions. The model consists in the use of a very well known solid state reaction such as the spinel formation starting from the parents oxides, the use of one of the two reactants in form of very thin films and the combination of several techniques based on synchrotron radiation.

The use of this strategy allowed an improvement of our understanding on the kinetics and mechanisms of these kind of reactions, in particular in the very first stages where, till now, nothing is known because of the lack of an adequate probe and an experimental strategy.

Once we have understood how the first stages work it will be easier to use these knowledges both for technological applications (such as nanoscience, for example) and for a better understanding of a lot of natural processes.

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