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Title	A POSSIBILITY OF INVESTIGATING SURFACE CHEMICAL REACTIONS
Author(s)	PESHEV, O.
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 19(3), 181-184
Issue Date	1971-12
Doc URL	https://hdl.handle.net/2115/24930
Type	departmental bulletin paper
File Information	19(3)_P181-184.pdf



(Note)

A POSSIBILITY OF INVESTIGATING SURFACE CHEMICAL REACTIONS

By

O. PESHEV*)

(Received June 29, 1971)

Recent progress in experimental methods allows the use of combined technique in the simultaneous study of the kinetics of a surface reaction and the alterations, provoked by it in the electro-physical properties of the surface. The combination of a quartz-crystal microbalance (QCMB) with a set up for measuring field effect (FE) in a thin, nearly single-crystal, semiconductor film would be of special interest. Herewith, we are attempting to give some considerations for the feasibility of a combination of this kind and state the possibilities it would offer in the investigation of chemisorption and catalytic phenomena.

The QCMB proposed by SAUERBREY¹⁾ is now a standard device for measuring the mass of thin solid films, with an area of the order of 1 cm² and an effective thickness varying from several hundredths to tens of thousands Å. It is capable of detecting a mass change of the order of 10⁻⁹ g/cm² and displays high stability (frequency drift less than 1 Hz over a day). Readings are virtually continuous, which is favorable for kinetics measurements: with a measuring time of 1 sec, the error is 1 Hz (a frequency drift of 1 Hz is easily resolved)¹⁾⁻³⁾. Though few in number, the reported investigations prove that the QCMB is applicable in studying surface chemical reactions³⁾⁻⁸⁾. It allows for example the direct measurement of a quantity, adsorbed on a total area of the order of 1 cm², thus making possible the adsorption study of specific crystal faces⁹⁾ and linking these results with the parallel alteration in the electronic properties of the surface. Precisely for the purpose of adsorption measurements, the role of the factors contributing to the error (*i.e.* temperature dependence of frequency, losses due to acoustic viscosity of the ambient gas, effect of the latter upon capacitance) has thoroughly been analyzed in ref.⁸⁾.

FE may be employed, as known, in determining the density and position (on the scale of energy) of the surface electronic levels (defects of adsorptive and

*) Higher Institute of Natural Sciences "P. Khilendarski", Plovdiv, Bulgaria.

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non-adsorptive origin). The technique of measuring FE in thin semi-conductor films including preparation and mounting of the samples has already been elaborated, as well as a way to interpret obtained data¹⁰⁾⁻¹²⁾. However, the technique cited offers no possibility of continuous tracing of the energy spectrum of the surface in the course of physico-chemical influence exerted upon it. This can be done by means of a set-up, created specially for this purpose by LITOVCHENKO *et al.*^{13),14)}. These authors use a scheme, allowing a simultaneous record of the curves of differential and integral FE in continuous regime. The position of the minima in the curves of differential FE shows directly the energy of activation of the surface centers, while the depth of these minima confers the latter's concentration. As the scanning of the entire energy interval lasts but mere seconds, the technique proposed by LITOVCHENKO *et al.* permits a detailed study of the changes in the spectrum of electronic states of the surface with time.

A multitude of techniques have been developed to prepare polycrystalline and nearly-single-crystal films of all type of materials¹⁵⁾. Epitaxially grown films consist of a number of large crystallites with very low angle grain boundaries¹⁵⁾. Such films are sometimes referred to as "single-crystal" ones, not in the strict sense of the word of course. The investigations of MANY *et al.*¹⁰⁾ have shown that vapour-grown films are quite suitable for FE measurements in a gas atmosphere. To combine these two schemes (the first one employing a QCM and registering the kinetics of alteration of mass with the second one, which by measuring FE records the change in the energy spectrum of the surface with time) seems quite possible. Nevertheless, in contrast to the case when one measures only the thickness (mass) of the thin solid film, the layer should not be applied directly on the electrode of the quartz-crystal oscillator, but should be separated from it by a thin insulating film. Thus, the investigated phenomena: changes of mass and of the energy spectrum of the surface, coincide in space, whereas their corresponding measuring schemes are electrically isolated. As regards the quality of the dielectric substrate, mica is of special interest, because it can be cleaved down to a thickness of some hundreds of Å¹⁶⁾. The sandwich-form "dielectric-semiconductor" could be attached to the electrode of the quartz-crystal oscillator with a suitable glue. Growing the epitaxial film separately on a mica substrate prevents from undesirable heating of the quartz-crystal.

The combined technique proposed here offers the possibility of simultaneously recording the course of a given surface reaction, taking place on a specified face of the single crystal, both gravimetrically and by the change in the electro-physical properties of the thin semiconductor film. The crystal orientation, stoichiometry and thickness of that film can be controlled and governed. Hence, we have all the possibility of studying the effect of these factors upon its chemisorption and

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catalytic behaviour. Thin films (10^{-5} – 10^{-4} cm) are rather feasible in investigating the influence of dispersity^{17),18)}, their thickness being of the order of the Debye screening length. FE measurements^{10),13)} allow the experimental study of the problem of electronic equilibrium of the surface during chemisorption. Theoretical investigations have shown that a number of characteristic features of chemisorption on semiconductors depend on the regime under which it proceeds, with or without preservation of the electronic equilibrium¹⁹⁾. There is also the problem of whether chemisorbed particles are surface defects, *i.e.* local chemisorption levels, with all causes following, such as change in conductivity and alteration of the work function²⁰⁾, or these are imitated by the circumstance that the chemisorbed particles alter only the spectrum of surface defects of non-adsorptive origin²¹⁾. If chemisorption kinetics are juxtaposed with the evolution in distribution of surface defects along the scale of energy, *i.e.* according to their position on the band picture, we could obtain a direct answer to that question.

The author wishes to thank Prof. G. BLIZNAKOV and Dr. K. STAMENOV for helpful advice and discussion.

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