Insulating Films on Semi- conductors

Editors: M. Schulz and G. Pensl

55

8262329

Insulating Films on Semiconductors

Proceedings of the Second International
Conference, INFOS 81,
Erlangen, Fed. Rep. of Germany,
April 27–29, 1981

Editors: M. Schulz and G. Pensl

With 240 Figures

Springer-Verlag Berlin Heidelberg New York 1981

Professor Dr. Max J. Schulz · Dr. Gerhard Pensl

Institut für Angewandte Physik, Universität Erlangen-Nürnberg, Glückstraße 9,
D-8520 Erlangen, Fed. Rep. of Germany

Series Editors:

Professor Dr. Günter Ecker

Ruhr-Universität Bochum, Theoretische Physik, Lehrstuhl I,
Universitätsstrasse 150, D-4630 Bochum-Querenburg, Fed. Rep. of Germany

Professor Dr. Walter Engl

Institut für Theoretische Elektrotechnik,
Rhein.-Westf. Technische Hochschule, Templergraben 55,
D-5100 Aachen, Fed. Rep. of Germany

Professor Leopold B. Felsen Ph.D.

Polytechnic Institute of New York, 333 Jay Street, Brooklyn, NY 11201, USA

Springer Series in Electrophysics
Volume 7

Springer Series in Electrophysics

Editors: Günter Ecker   Walter Engl   Leopold B. Felsen

Preface

The INFOS 81 Conference on Insulating Films on Semiconductors was held at the University of Erlangen-Nürnberg in Erlangen from 27 to 29 April 1981. This conference was a sequel to the first conference INFOS 79 held in Durham. INFOS 81 attracted 170 participants from universities, research institutes and industry. Attendants were registered from 15 nations. The biannual topical conference series will be continued by INFOS 83 to be held in Eindhoven, The Netherlands, in April 1983.

The conference proceedings include all the invited (9) and contributed (42) papers presented at the meeting. The topics range from the basic physical understanding of the properties of insulating films and their interface to semiconductors to the discussion of stability and dielectric strength as well as growing and deposition techniques which are relevant for technical applications. Strong emphasis was given to the semiconductor silicon and its native oxide; however, sessions on compound semiconductors and other insulating films also raised strong interest. The proceedings survey the present state of our understanding of the system of insulating films on semiconductors. As a new aspect of the topic, the properties of semiconductors deposited and laser processed on insulating films was included for the first time.

The organisational load of the conference was distributed on many collaborators. The service of the session chairmen who together with many participants reviewed all the publication manuscripts during the conference, was very much appreciated. Special thanks go to all the colleagues and students of the Institute of Applied Physics who assisted in the local organization. The conference administration and the retyping of many manuscripts in the proceedings was performed with great care and engagement by Mrs. Gabriele Loy. All the help is gratefully acknowledged.

Erlangen, April 1981   *M.Schulz · G.Pensl*

8262329

Contents

Part VII   Technology

Part VIII   Laser Processing

Part IX   Transport Properties in Inversion Layers

Part I:

Si–SiO$_2$ Interface

Electronic Structure of the Si–SiO$_2$ Interface

Frank Herman

IBM Research Laboratory
San Jose, CA 95193, USA

After sketching various theoretical models that have been proposed for de-
scribing the Si/SiO$_2$ interface on an atomic scale, we will discuss an ideal-
ized model which is designed to simulate the average contact between a silicon
crystal and its oxide overlayer. According to this model, the Si/SiO$_2$ inter-
face is represented by the boundary between two crystalline domains, the first
being the silicon substrate, and the second an idealized crystalline form of
SiO$_2$, diamond-like beta cristobalite. Nearly perfect registry between Si and
SiO$_2$ is obtained by placing the (100) face of the former next to the 45° ro-
tated (100) face of the latter. Half the Si atoms at the interface are four-
fold coordinated, connecting the Si and SiO$_2$ regions to one another. The re-
maining half are connected only to the silicon substrate and are thus twofold
coordinated. Localized electronic states in the thermal gap at the interface
are associated with the dangling bonds at the twofold coordinated Si atoms.
If H, O, or OH groups are attached to these Si atoms, eliminating the dan-
gling bonds, the thermal gap interface states are also eliminated. Even though
this model ignores structural disorder, it does provide considerable insight
into the nature of the Si/SiO$_2$ interface. We will discuss some of the implica-
tions of this model, as well as the results of model-based theoretical cal-
culations. In particular, we will consider the electronic structure of the
interface including the effects produced by the introduction of Si and O va-
cancies and interstitials and other types of localized defects.

1. Introduction

Because of the important role played by the Si/SiO$_2$ interface in modern semi-
conductor technology, considerable experimental and theoretical effort has
been devoted to the study of this interface [2-8]. Oxidation of a silicon sur-
face produces an amorphous oxide layer whose atomic arrangement is not well

2

understood. Many authors have suggested that there is a non-stoichiometric transition layer, often described as SiO_x, separating the silicon substrate from the stoichiometric SiO_2 layer. (Here x lies between 1 and 2.) The detailed atomic structure of the transition layer, including its uniformity and width, its structural disorder, its affinity for impurity atoms, etc., continues to be a subject of debate. Of course, the nature of the transition layer is expected to depend on the manner in which the oxide layer is formed. By the same token, a better understanding of the transition layer could lead to further improvements in the preparation of Si/SiO_2 interfaces.

The technological importance of the Si/SiO_2 interface arises from the fortunate circumstance that suitably oxidized silicon substrates are protected from environmental contaminants and have rather low densities of localized interface states in the thermal gap. There continues to be considerable interest in the nature and identity of the residual defects that occur near well-prepared interfaces, giving rise to residual trapping sites and fixed charge. Many imaginative models of defects at the Si/SiO_2 interface and in SiO_2 have been proposed [2-11], but relatively few of these defects have been unambiguously identified, even by such precise measurements as ESR [11]. In view of the difficulties encountered in practice in attempting to interpret most experimental measurements in terms of specific defects, we thought it would be useful to develop a simple model for the Si/SiO_2 interface which could provide a conceptual framework for thinking about interface defects as well as a theoretical framework for carrying out numerical calculations.

In the first paper on this subject [12], we described the construction of idealized Si/SiO_2 interfaces and superlattices and demonstrated by first-principles band structure calculations that there are no localized interface states in the thermal gap if all the Si atoms at the interface are saturated. In a second paper [13] we showed how localized defects in SiO_2 could be investigated theoretically by introducing periodic arrays of noninteracting defects in a SiO_2 supercell normally containing 24 atoms. In a third paper [14] we introduced periodic arrays of noninteracting defects in idealized Si/SiO_2 superlattices, thereby simulating the presence of localized defects at or near the Si/SiO_2 interface. In the present paper we will first mention some recent attempts by others to develop a theoretical model of SiO_2 and the Si/SiO_2 interface, and then we will discuss our own model briefly and summarize some of our principal conclusions.

3

2. Theoretical Models of the Si/SiO$_2$ Interface

The extensive literature on crystalline and non-crystalline SiO$_2$ and on Si/SiO$_2$ interfaces [2-11] contains a variety of models of the oxide layer and the Si/SiO$_2$ interface. In this paper, we will focus on atomic scale rather than on phenomenological models. Nearly all the models that have been proposed for describing the atomic arrangements at the interface are speculative. Some of the proposals are quite specific. They assume particular types of linkages between Si and SiO$_2$, well-defined structural imperfections arising from modifications in the normal linkages, as well as chemical imperfections due to the presence of specific foreign species. The remaining proposals tend to be descriptive or impressionistic, invoking dislocations, disjunctions, varying degrees of stoichiometry and crystallinity, etc. The first set of proposals can be distinguished from the second by the ease with which ball-and-stick models can be constructed to illustrate the proposed arrangements.

There has also been considerable debate regarding the initial formation of the oxide layer, and how this layer might change as it grows [2-8]. Some authors believe that a better understanding of the initial stages of oxidation could provide valuable clues concerning the nature of the ultimate oxide layer; other authors disagree. In any event, it is very important to have heuristic atomic models of the formation and ultimate structure of the Si/SiO$_2$ interface, because such ideas could lead to improved processing techniques, new device concepts, and better understanding of still more complex semiconductor/insulator interfaces.

Up to now, most Si/SiO$_2$ interface modeling studies have been qualitative, being based on simple physical and chemical reasoning. Many of the arguments put forward in favor of specific atomic models seem quite plausible, but it is usually difficult to verify these interface models experimentally. Therefore, a constructive step would be to study some of these models theoretically and obtain quantitative estimates of crucial electronic properties. If one wishes to carry out detailed electronic structure calculations for model systems, it is obviously necessary to have specific atomic arrangements in mind. The essential difficulty is that we do not know the actual structure of the Si/SiO$_2$ interface on an atomic scale.

The overall problem can be dealt with in three parts: In the first and easiest part, one makes certain assumptions about the silicon substrate. For example, one chooses a specific crystalline orientation, and then assumes that the silicon is structurally perfect up to the interface. Relaxation and reconstruction effects can be deferred to a later stage or expressly ignored.

The second part concerns the description of the oxide film property, allowing if possible for its noncrystalline nature. In dealing with non-crystalline SiO_2, one can build on our improved knowledge of amorphous and glassy semi-conductors [9,15-19]. The third part, the most difficult of all, involves connecting the silicon substrate to the non-crystalline oxide layer in a physically and chemically plausible manner.

One popular model for noncrystalline SiO_2 and the Si/SiO_2 interface is the cluster Bethe lattice model [20,21], which takes topological aspects of structural disorder into account in an elegant manner. Because this model is rather simple in form and can be easily parameterized, it can be used to study electronic and lattice vibrational spectral properties associated with ideal and defective interfaces. But because these models are based on adjustable parameters that are assigned ad hoc values, they are not particularly trustworthy from a quantitative point of view [22]. Nevertheless, they do have considerable pedagogical value.

Another popular model of non-crystalline SiO_2 is the continuous random network model [15-19], according to which SiO_2 is composed of a randomly oriented collection of SiO_4 tetrahedra which are linked to one another to form a continuous network of Si-O-Si bonds. It is assumed that the SiO_4 tetrahedra tend to maintain their structural integrity (bond lengths and bond angles) in different environments, and that the necessary structural versatility is provided by the Si-O-Si bond, whose angle may assume a wide range of values at little cost in energy [4]. Models of this type have recently been used to study bulk SiO_2 [23] as well as the Si/SiO_2 interface [24]. In the study of bulk SiO_2, cyclic boundary conditions were imposed on a large disordered molecular SiO_2 cluster, producing a computationally tractable model of non-crystalline SiO_2. The object here was to investigate electron and hole localization induced by the structural disorder.

In the study of the Si/SiO_2 interface, it was demonstrated that a rather abrupt interface could be constructed within the framework of a continuous random network model, a rather important result. Unfortunately, the resulting atomic model is much too complex for detailed electronic structure studies. In both [23] and [24], the construction of continuous random network models is based on ideas regarding the nature of non-crystallinity which are highly subjective and which may not necessarily describe the experimental situation. It is possible that non-crystalline SiO_2 near a Si/SiO_2 interface does not actually form a completely continuous random network. That is to say, the network may contain discontinuous elements such as non-bridging O atoms or three-

5

fold coordinated Si atoms connected to H or OH groups, or voids composed of aggregates of such discontinuous elements [19].

There are many theoretical efforts currently underway [18,19,25] whose aim is to formulate general guiding principles for constructing atomic models of non-crystalline materials. Combined with intuitive notions [26] and computer modeling [27,28], these theoretical studies may eventually lead us to objective models which we can use with confidence for electronic structure studies of non-crystalline SiO_2. In the meanwhile, the atomic architecture of the Si/ SiO_2 interface remains an open question.

We already know from extensive experimental and theoretical studies [2,3, 29] that the gross features of the electronic structure of non-crystalline and various crystalline forms of SiO_2 are essentially the same, reflecting the common SiO_4 building block. Only the finer details of electronic structure are affected by the special manner in which the SiO_4 tetrahedra are linked together in a particular structural modification. In view of the overwhelming importance of the short-range order (linked SiO_4 tetrahedra) in determining the essential features of the electronic structure of SiO_2, and the likelihood that the long-range disorder affects only the finer details, we will explicitly ignore the structural disorder of SiO_2 and concentrate on models of the interface which represent the average contact between Si and SiO_2.

3. Idealized Si/SiO_2 Superlattices and Interfaces

Our overall program is as follows. First, we will disregard structural disorder in SiO_2, and represent SiO_2 by a suitably chosen periodic structure. We will then form ordered Si/SiO_2 interfaces by attaching crystalline SiO_2 to crystalline Si. Next, we will construct a Si/SiO_2 superlattice by stacking Si and SiO_2 slabs on top of one another. The slabs will be made sufficiently thick so that successive interfaces will not interact with one another. Because the Si/SiO_2 superlattice is a periodic structure in three dimensions, we can use the highly developed methods of band theory [30] to calculate the electronic structure. The results of such calculations include a description of localized interface states, including their energy levels and charge distributions. Finally, we can introduce structural and chemical imperfections, and study their effects on the electronic structure.

To carry out the above program, we begin by representing the oxide layer by an idealized crystalline form of SiO_2 having as simple a unit cell as pos-
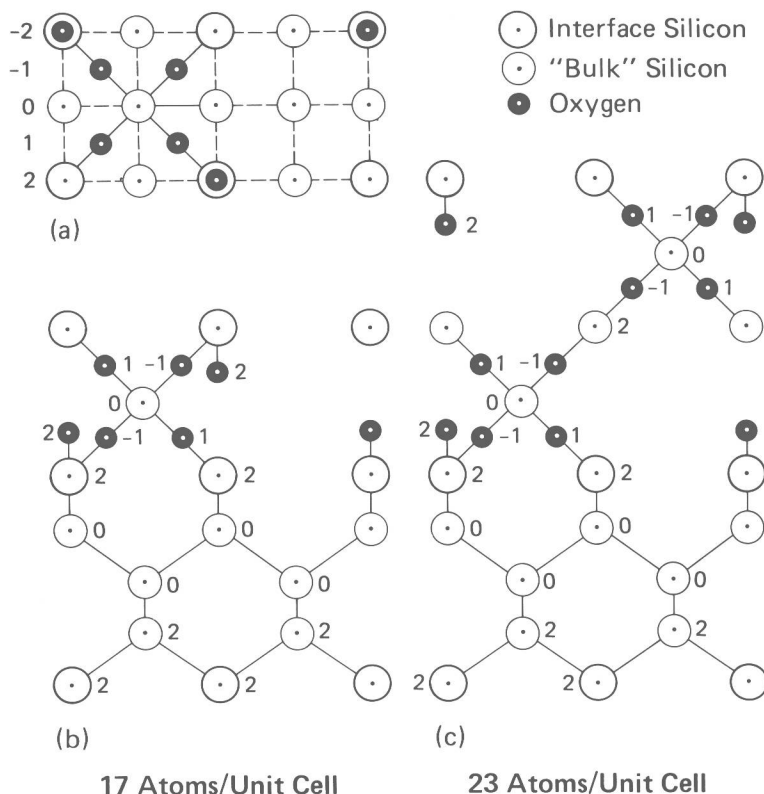
Fig. 1a-c. Si/SiO₂ superlattices and interfaces. Panels (a) and (b) depict
the top and front views of a superlattice having 17 atoms per unit cell, and
panel (c) depicts the front view of a superlattice having 23 atoms per unit
cell. Both superlattices have five layers of silicon (2 atoms each) and two
oxygen atoms saturating the twofold coordinated Si substrate atoms. In panel
(b) there is one tier of SiO_4 tetrahedra (5 atoms), while in panel (c) there
are three SiO_4 tiers (11 atoms). The numbers denote the planes in which the
various atoms lie, the 2 representing the front-most plane, etc. Another view
of these superlattices appears in [8]

sible. For this purpose we will use beta cristobalite [31], except that we
will straighten out the Si-O-Si bonds in the actual structure, making them
all linear rather than crooked (all bond angles 180° rather than about 140°).
Assuming an Si-O bond length of 1.633 Å [32], the linear Si-O-Si bond length
becomes twice this, and the unit cube edge of idealized diamond-like SiO_2 be-
comes 7.543 Å, which is 5 percent larger than the unit cube edge of actual
beta cristobalite, 7.16 Å. This 5 percent difference reflects the contraction
produced by the bent bonds in the actual structure. Except as otherwise noted,