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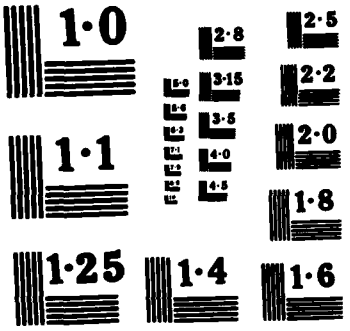

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The primary focus of this work was the exploration of fundamental aspects of the oxidation of semiconductor surfaces with a view to addressing some of the problems that have arisen in industry in the growth of ultra thin silicon dioxide layers that are a requirement for smaller, faster CMOS devices. The work falls into three categories, each concerned with a problem that is related to the central issue in a different way: (1) A study of the fundamental properties of the diamond surface. (2) A study of rare earth metal/semiconductor interfaces and compounds. (abstract cont'd)

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20. ABSTRACT CONTINUED:

(3). A study of the fundamental characteristics of the oxidation of silicon and the production of thin silicon oxide layers.

Keywords included

19

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NOVEL APPROACHES TO PASSIVATION OF Si for VHSIC - BASED ON FUNDAMENTAL STUDIES

Final Report

W. E. Spicer, I. Lindau, and J. Nogami

May 24, 1985

U. S. Army Research Office

Stanford University

Stanford, CA 94305

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Final Report for ARO contract DAAG 29-82-K0087

A. Statement of the problem studied

The primary focus of the work done under this proposal was to explore fundamental aspects of the oxidation of semiconductor surfaces with an eye towards addressing some of the problems that have arisen in industry in the growth of ultra thin SiO_2 layers that are a requirement for smaller, faster CMOS devices. The work falls into three categories, each concerned with a problem that is related to the central issue in a different way.

The first is a study of the fundamental properties of the diamond surface. Diamond can be treated as a prototypical semiconductor with a large band gap; many aspects of the behaviour of its surface and its interaction with gas adsorbates and metal overlayers can be directly compared with silicon and germanium, and can allow the understanding of analogous behaviour of these different semiconductor substrates. The study of diamond is important is deliniating the effects due to the covalent bonding and crystal symmetry, which is the same for all three materials, from the effects of band gap, which is very different. This work was a continuation of a project carried out under a research contract of which this contract was an extension. The project was completed under this contract. The results comprise the PhD thesis of Brad Pate.

The second area of work is a study of rare earth metal / semiconductor interfaces and compounds. These systems have attracted recent interest beacuse rare earth silicide/Si junctions have the lowest reported Schottky barrier heights for contacts on n-type silicon. This low barrier opens the possibility of making more efficient Schottky barrier infrared imaging devices. The corresponding high barrier to p-type has application in MESFET structures on p-Si, and in complementary MESFET structures which could have advantages over conventional CMOS in very dense VLSI. MESFET structures do not require an oxide layer to insulate the gate, which is difficult to produce as the device size gets very small. This work will comprise the PhD thesis of Jun Nogami.

The third area is concerned with the fundamental characteristics of the oxidation of Si and the production of thin Si oxide layers. The oxidation of Si wafers was studied as a function of substrate temperature and oxygen exposure. Additional work was initiated on the production of oxide layers via silicon MBE techniques: specifically the deposition of Si onto a heated substrate under an ambient oxygen atmosphere. The oxide produced was compared with the results from oxidation of the Si substrate.

B. Summary of important results

The diamond surface

The work on the diamond surface demonstrated for the first time the importance of hydrogen termination on the behavior of the surface, and resolved apparent inconsistencies in previously reported results.

The principal results are as follows:

- The clean diamond (111) surface has a 2x2 or 2x1 reconstruction. This reconstruction becomes 1x1 when the surface is hydrogen terminated.
- For the clean (111) surface, the C 1s core level exhibits a surface shift of ~0.9 eV to lower binding energy with respect to the bulk value. This is the first report of a surface shift for diamond. Exposure to hydrogen returns the surface atom binding energy to the bulk value.
- The near edge structure of the C 1s threshold exhibits a surface core exiton that is consistent with the existence of empty π anti-bonding orbitals as predicted by the Pandey π-bonded chain model of the diamond (111) 2x2/2x1 surface. However, this feature is not significantly affected by hydrogenation of the surface, indicating that the degree of π-bonding at the surface is unchanged by hydrogenation.
- The effect of Al deposition on the surface was studied. Interaction with Al appears to shift the C 1s level to lower binding energies, to the position of the surface shifted peak observed on the clean surface. Annealing drives the Al into the surface and increases the magnitude of the shifted peak.

Rare earth metal / semiconductor interfaces and compounds

Rare earth metal / semiconductor interfaces and compounds have been studied in only recent years and a general picture of their behaviour has just begun to emerge. Such diverse phenomena as reactive interdiffusion, mixed valence, surface valence change, ordered annealed phases, clustering, segregation and low Schottky barrier height have all been observed in these systems under different circumstances with different experimental techniques. The work carried out under this contract is an extension of a continuing program of study of metal silicide/silicon systems, and is a logical extension of previous work on transition metal and refractory metal systems.

Our research in this area has been directed primarily towards understanding the formation of these interfaces at room temperature. Studying the electronic structure of these interfaces and related compounds, we can address such issues as the behaviour at the initial stages of interface formation, the nature of the bonding between the R.E. metal and the semiconductor, and the influence of both chemical and atomic environment on the highly localized 4f levels that overlie the valence band region.

At this point in time, we have studied interface formation for three different metals on Silicon substrates: Ytterbium, Europium and Gadolinium, both at room temperature and elevated temperatures In addition, we have studied three bulk Yb silicides, and the Yb/Ge interface to broaden the basis on which we can interpret the results for the Yb/Si interface in particular.

There are three stable compounds in the Ytterbium/Silicon system: Yb_5Si_3, YbSi and Yb_3Si_5. As part of the research sponsored by this contract, we have studied the electronic structure of these binary rare earth silicides using synchrotron radiation photoelectron spectroscopy on well-characterized bulk samples. Trends in the electronic structure as a function of the stoichiometry provide information on the nature of the bonding in these compounds and the influence of environment on the behaviour of the individual atoms. Such information is crucial to the understanding of the electronic structure of each individual compound, and in addition facilitates the interpretation of the complex evolution in electronic structure observed at rare earth / Si interfaces, both at room temperature and at elevated temperatures.

All four interface systems share many common features in their behavior:

- At room temperature, the metal atoms react with the substrate to varying degrees at very low coverages (e.g. 0.2 monolayers). The interface formed at room temperature is narrow, with intermixing and reaction limited to between 3 and 5 atomic layers. The interfacial region itself appears to be a Si (Ge) poor silicide (germanide) that is stable with further metal deposition.

- No change in rare earth valence is observed at the interface at room temperature. Mild heating (temperatures as low as 200°C) strongly enhances reaction and interdiffusion.

- For the case of Yb films annealed on Si substrates, it is possible to produce both Yb-rich phases that are divalent, and mixed valent phases with a higher relative concentration of Si. It is important to note that all such annealed phases were observed to be inhomogeneous and were not indentifiable as being any of the known silicides in the Yb/Si system.

- For Eu on Si, annealing did not produce any valence change, although reaction with Si was strongly enhanced.

- The Schottky barrier height for all three metals on n-type Si was low, and in agreement with electrical measurements made elsewhere.

For the bulk silicide spectroscopy, the prinicipal results are as follows:

- There is a non-monotonic trend in the valence ratio with stoichiometry. Yb_5Si_3 is divalent, Yb_3Si_5 and YbSi mixed valent, but YbSi has the higher proportion of trivalent to divalent Ytterbium.

- There is a chemical shift of both the Si 2p and the Yb 4f core levels towards lower binding energy in the silicides that increases with increasing Si concentration. In the mixed valence silicides, the 4f levels shift and cross the Fermi level. In comparision with Yb_3Si_5, YbSi has both a lower 4f emission at the Fermi level and a higher proportion of Yb^{3+} emission.

- The surface shift in the Yb^{2+} 4f structure is larger for all three compounds than it is in Yb metal and in fact increases with decreasing relative concentration of Yb. This has been observed in other similar Yb compounds.

- For both the mixed valence silicides, the observed valence ratio Yb^{3+}/Yb^{2+} increases with increasing photon energy (and decreasing surface sensitivity of measurement). In Yb_3Si_5, this trend can be fit by a simple model in which the first atomic layer of Yb is entirely divalent.

The oxidation of the Si(111) surface

The primary focus of this study was the initial stages of oxidation of the Si surface at elevated temperatures, and the production of thin Si oxide layers, both by oxidation and by deposition of Si onto a Si substrate under an ambient of oxygen. Many previous studies on the oxidation of Si have concentrated on the behavior at room temperature. Our intention was to study the growth of oxide layers under conditions more close to those in industry.

For the oxidation of the Si(111) surface at elevated temperatures, the substrate temperature was varied from room temperature to 800°C, and the oxygen exposure from 0L to 1000L. (1L = 10^{-6} torr sec). The principal results were as follows:

- Under the above range of conditions, oxide layer thickness varied from 0 to 3 monolayers.

- For room temperature oxidation, the oxide growth rate flattened out after an initial stage of fast growth. This transition in oxidation rate occurred at one monolayer (ML) oxide thickness. This result is consistent with previous work done elsewhere.

- At the transition point, LEED shows that the surface order changes from 7x7 to 1x1, the surface states disappear, and there is a shifted component of the Si 2p core level that can be associated with Si atoms on the surface with an oxygen atom at the ontop site, saturating the dangling bond.

- At elevated substrate temperatures, the silicon was more completely oxidized. This was manifested in two ways: the increasing shift of the reacted component of the Si 2p core level with increasing temperature, and the details of the valence band structure as observed by photoemission spectra taken at lower photon energies (21.2 eV). The oxide became SiO_2 at the highest temperature and oxygen exposures studied.

- Plotting the LEED results in a map of oxygen exposure vs oxidation temperature yields three distinct areas of different surface order: a 7x7 region associated with overlayers with the least relative oxygen content, a 1x1 transition region around 1ML oxygen coverage, and a region of amorphous surface associated with SiO_2. These three regions exhibited very different Si/O ratios. Growth at low temperature and high oxygen exposure resulted in amorphous overlayers. Growth at the highest temperatures studied exhibited 7x7 surface order until the very highest oxygen exposure.

- The map of oxide layer characteristics versus temperature and exposure enabled the definition of growth conditions under which it should be possible to grow oxide layers with 1x1 surface order using Si deposition during oxidation. Other work has shown that these ordered silicon oxide layers are semi-insulating and that it is possible to grow epitaxial Si on top of them. The potential applications for the capability of producing insulating layers between crystalline Si layers is quite broad, and can lead to new semiconductor / insulator junction device structures.

C. Publications

"Photoemission and Photon Stimulated Ion Desorption Studies of Diamond (111): Hydrogen"
B.B.Pate, M.H.Hecht, C.Binns, I.Lindau and W.E.Spicer
J. Vac. Sci. Technol. 21(2), 364 (1982)

"The Diamond (111) surface: a dilemma resolved"
B.B.Pate, B.J.Waclawski, P.M.Stefan, C.Binns, T.Ohta, M.H.Hecht, P.J.Jupiter, M.L.Shek, D.T.Pierce, N.Swanson, R.J.Celotta, I.Lindau, and W.E.Spicer
Physica B 117B&118B, Proc 16th Int. Conf. Phys. Semiconductors, (1982)

"The Diamond Surface: Atomic and Electronic Structure"
B.B.Pate
to appear in Surf. Sci.

"Very Strong Lattice Coupling in Diamond at Photon Energies up to 1.5 eV above the Bandgap"
B.B.Pate, I.Lindau, and W.E.Spicer
Proc. 17th ICPS, (1985) in press

"Photoemission Spectroscopy of the Si/Eu Interface Using Synchrotron Radiation"
J.Nogami, C.Carbone, J.J.Yeh, I.Lindau, and S.Nannarone
Proc. 17th ICPS, (1985) in press

"The Silicon/Gadolinium Interface at Room Temperature"
C.Carbone, J.Nogami, and I.Lindau
to appear in J.Vac.Sci.Technol.

"Photoemission Studies of Yb_3Si_5: Bulk and Surface Spectroscopy"
I.Abbati, L.Braicovich, U.del Pennino, C.Carbone, J.Nogami, J.J.Yeh, I.Lindau, A.Iandelli, G.L.Olcese, and A.Palenzona
submitted to Phys. Rev. B

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