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Electrochemistry and Structures of Silicon Surface

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Abstract: Accurate control and fabrication of silicon surface structures from atomic scale to micrometer scale, which may be randomly associated with surface roughness or have well defined patterns, is critical for the performance and reliability of electronic devices Electrochemical reactions of silicon in solutions involved in wet cleaning and etching of silicon wafer play an important role in determining the structures of silicon surface. A tremendous amount of researches have been done in the last several decades to understand and control a range of complex electrochemical reactions at silicon/solution interface and their relations to the resulted surface structures The findings generated from these research efforts have been compiled and integrated in a recently published book. This paper is to present an overview, using synthesized information from this book, on the aspect of silicon dissolution and the resulted surface structures

Key words: Silicon, Etching, Dissolution, Surface structure, Micro device fabrication, Surface reactions, MEMS

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1　Diversity of Electrode Phenomena

The functionality of most modern electronic devices and micro electromechanical systems (MEMS) are realized by the micro structures on silicon surface. Electrochemical reactions of silicon are commonly involved in wet cleaning and etching of silicon wafer for control and manufacturing structures on silicon surface[1-3]. The phenomena that can be generated by the electrochemical reactions on single crystalline silicon electrodes are diverse, including oxide formation and passivation, current oscillation, anisotropic etching, formation of porous silicon etc. Each of these phenomena has extremely rich details with complex relationships between structures and properties of silicon electrodes and between properties and experimental conditions

The physical and chemical nature of the silicon/electrolyte interface, in terms of carrier type and density, charge distribution and transfer, surface reactions, evolution of surface geometry, etc. are determined by numerous variables as illustrated in Fig 1[3]. Each of these variables is a continuum of a wide dimensional range and its effect on the electrode properties involves time and micro surface geometry. Thus, the possible conditions determined by the combinations of these variables are limitless, responsible for the diverse phenomena and complex details observed on silicon electrodes These possibilities also form the basis for the cleaning and etching processes that are widely utilized in the fabrication of electronic devices Reactions and surface structures are mutually related: reactions generally result in forming and changing of surface structures while surface structures determine the nature and distribution reactions

2　Dissolution Reactions

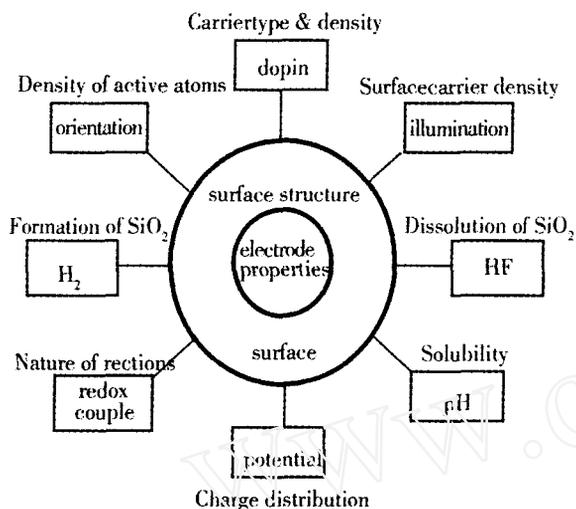In the absence of redox couples other than those

Fig 1   The major variables that affect the electrochemical properties of silicon electrode

associated with water and silicon, the electrochemical reactions on silicon in aqueous solutions are dominated by either silicon dissolution, or oxide formation and dissolution, or hydrogen evolution depending on the potential range and solution composition.

The dissolution of silicon can be best characterized by i-V curves Neglecting the details associated with silicon substrate such as doping, the current-potential relationship of silicon in aqueous solutions can be considered to be principally determined by the pH and HF concentration as illustrated in Fig 2[3-5]. In non-alkaline and non-fluoride aqueous solutions, silicon as an electrode is essentially inert showing a very small current at anodic potential due to the presence
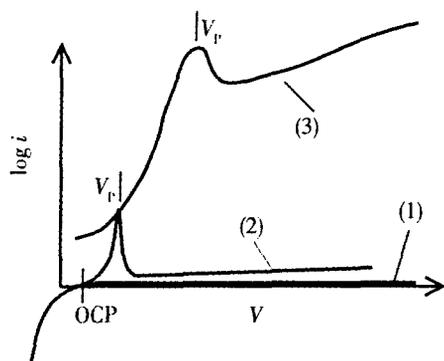

YFig 2   The typical i-V cures for silicon dissolved in HF(3), alkaline (2) and non-fluoride, non-alkaline solutions (1)

of a thin oxide film (curve 1). In alkaline solutions silicon is also passivated by an oxide film at anodic potentials but is active below the passivation potential V_P (curve 2). In fluoride solutions silicon electrode is active in the entire anodic region, indicated by the large anodic current(curve 3).

In non-HF aqueous solutions, the silicon surface is generally covered by an oxide film and in HF solutions the silicon surface tends to be terminated by hydrogen(in the form of hydrides). The formation of a surface hydride layer or oxide layer is responsible for the stability of silicon at open circuit potential(OCP) in aqueous solutions In HF solution, the surface is fully covered by an oxide film at anodic potentials higher than the passivation potential, while it is fully covered by hydrogen at potentials more negative of the open circuit potential From the open circuit potential to the passivation potential, the surface coverage of hydrogen gradually decreases as the coverage of oxide increases Also, while at potentials near the open circuit potential and below the passivation potential, the hydride or oxide layer is on the order of a monolayer, the hydride layer at the cathodic potentials and the oxide layer at potentials higher than the passivation potential is relatively thick. The difference in the kinetics for formation of a hydride layer and an oxide layer and in the stability of these two layers plays a critical role in the diverse phenomena observed on silicon electrodes

The i-V curves in HF solutions are different for p-Si and n-Si in the dark due to the difference in the concentrations of holes on the surface, of these two materials Large currents can be obtained on p-Si by anodic polarization to increase the concentration of holes at the surface. On the other hand, for non-degenerated n-Si the anode current is limited by the availability of holes The i-V curves for n-Si becomes identical to that of p-Si when n-Si is illuminated at a high light intensity.

Fig 3 shows that the current increases exponentially with increasing potential from OCP[6]. It breaks off from the exponential behaviour at larger overpotentials, exhibits a peak, J_1, and then attains a relative-

ly constant value at J_2. Examination of the surface anodized at different potentials, indicates that formation of porous silicon occurs in the exponential region but not at potentials more positive than the peak potential. The potential corresponding to the maximum slope of the i V curve is about the upper limit for formation of uniform porous silicon layer. At potentials between the maximum slope and the current peak, porous layer may still form but its surface coverage is not uniform. Visible hydrogen evolution occurs in HF solutions at anodic potentials in the exponential region anodic of OCP. The rate of hydrogen evolution substantially decreases as potential approaches the current peak, J_1. Hydrogen evolution ceases above the current peak.
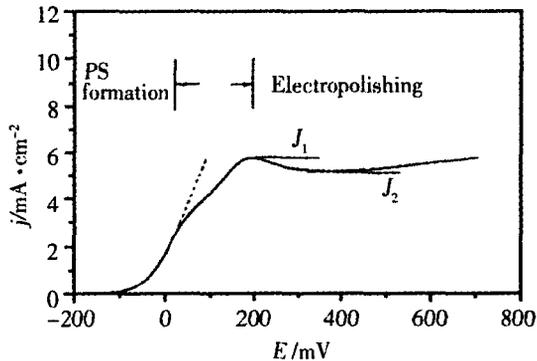

Fig 3   Current-potential curve of the p^+ silicon sample in 1% HF solution with potential sweep rate of 2 mV / s

In aqueous solutions at OCP in the absence of redox couples, hydrogen evolution is the only reduction reaction accompanying the dissolution of silicon[7-8]. Hydrogen evolution on silicon may proceed chemically or electrochemically depending on the conditions. In HF near OCP and at anodic potentials it proceeds completely chemically, i.e. without involving the carriers from the electrode. The chemical nature of hydrogen evolution is responsible for less than 4 of the silicon effective dissolution valence in HF solutions. Hydrogen evolution at cathodic potentials is predominantly electrochemical due to the lack of silicon dissolution and abundance of electrons on the surface of n-Si or illuminated p-Si.

In KOH at OCP and at anodic potentials lower than V_P, there is no participation of charge carriers and the reactions, hydrogen evolution and dissolution of silicon, are almost 100% chemical such that the etching of silicon is characterized with the dissolution of one silicon atom and the evolution of two hydrogen molecules. At potentials higher than V_P, the surface is passivated and both silicon dissolution and hydrogen evolution cease[9]. At cathodic potentials, hydrogen evolution on p-Si is also chemical due to the lack of electrons. However, for n-Si at cathodic potentials hydrogen evolution is mainly electrochemical due to the abundance of electrons from the semiconductor.

Many processes in different phases in the silicon / electrolyte interface region are involved during electrochemical reaction, Each of the possible processes, as schematically illustrated in Fig 4, in the multi-layer silicon / electrolyte interface region can be the rate limiting process under certain conditions, as has been summarized in reference [3]. For example, the anodic reaction processes on n-Si in the dark is limited by the minority hole transport in the bulk of silicon, that is r_2. For p-Si and illuminated n-Si in HF solutions at potentials negative or positive of the current peak, J_1, the reaction rate is determined by the charge transfer process across the electrode / electrolyte interface, that is, r_4 and r_5. At potentials positive of J_1, i.e. the electro polishing region, the rate determining step in the anodic reaction is the dissolution of the anodic oxide film, that is r_{10}. The dissolution of the oxides formed at low fluoride concentrations is mainly kinetically controlled, that is r_{10}, while for high fluoride concentrations the process is mainly diffusion controlled, r_{11}. There is a critical concentration, depending on pH, rotation rate and potential, at which the contributions by kinetic and diffusion processes are equal[8].

In KOH solutions the rate limiting process at OCP is of chemical nature, i.e. only r_6 is involved. The electrochemical processes, that is r_4 and r_5, are increasingly involved as potential is increased from OCP to V_P. At potential large than V_P, the anodic reaction is limited by the dissolution rate of the oxide,

r_{10} , which, unlike in fluoride solutions, is completely a surface controlled processes in KOH solutions
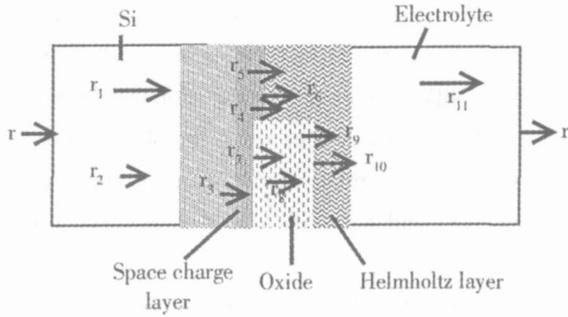

Fig 4   Schematic illustration of the processes involving the transport of charge and species in the different phases in the Si/electrolyte interface region

r_1) & r_2) majority&minority carrier transport, r_3) transport of holes to the surface, r_4) charge transfer across the Helmholtz layer, r_5) electron injection, r_6) chemical dissolution, r_7) oxide formation, r_8) ionic transport in oxide, r_9) injection of oxidants, r_{10}) dissolution of oxide, r_{11}) mass transport in electrolyte

3 Rate of Silicon Dissolution

The two principle etching solution systems for silicon are HF solutions and alkaline solutions[3]. This is because silicon is inert in aqueous solutions due to the formation an insoluble surface oxide, except for HF solutions or alkaline solutions in which the oxide is soluble. Various chemical agents can be added into these two solutions to control etch rate, etch selectivity, solution stability, and quality of the etched surface. One major difference between these two systems is that the etch rate of silicon in HF solutions is similar among the various crystalline orientations, i. e. isotropic, while in alkaline solutions it strongly depends on the crystalline orientation, that is anisotropic. Another difference is that silicon oxide, which may be present on silicon surface prior or during an etching process, etches fast in HF solutions while it etches very slowly in alkaline solutions relative to the etch rate of silicon.

Several general points may be made regarding etch rate of silicon: i) silicon can etch at a wide range of rates, as much as 9 orders of magnitude; ii)

the highest etch rates are observed in HF solutions; iii) the etch rates of the three major crystal planes vary only marginally in HF solutions but vary greatly in alkaline solutions; iv) etch rate is specific to a given set of etching conditions. In addition to material and solution conditions, the etch rate of silicon in a given system depends on many operational parameters such as size and geometry of the sample, volume of the solution, stirring condition, ambient (light and air) control and etching time. Thus, for a given silicon material and solution composition, etch rate may significantly vary when it is measured under different operating conditions. This is often responsible for the sometimes large difference in etch rates that can be found in identical systems from different investigations.
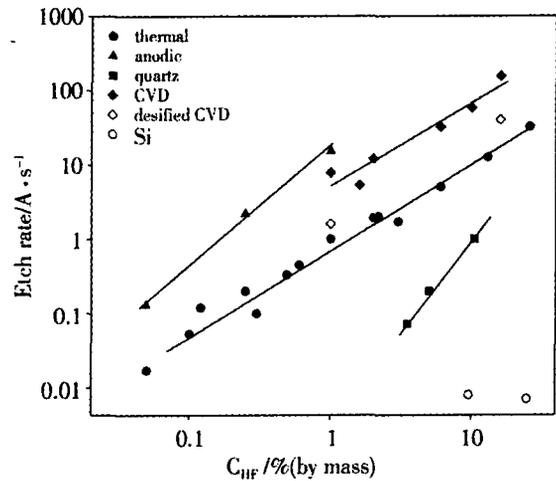

Fig 5   Etch rate of different silicon oxides as a function of HF concentration

The etching of silicon oxides is particularly important in silicon technology. Deposited silicon oxides are used as an dielectric layer, passive layer or masking materials for device fabrication and as a native oxide it is an essential part of the surface condition. In particular, the oxide formed on silicon during electrochemical processes plays a critical role in the properties of silicon electrode; most of the electrode phenomena observed on silicon are associated with the formation and dissolution kinetics and the properties of the surface oxides. Fig 7 shows the etch rate of different types of silicon oxides as a function of HF concentra-

tion. Several general remarks can be made on the data: 1） Etch rate of all the oxides increases with HF concentration; 2） The etch rates differ by several orders of magnitudes for different types of oxides with quartz being the slowest and anodic oxide being the fastest, reflecting the large difference in the structure of these oxides; 3) silicon as a solid is extremely stable in HF solutions compared to its oxide, as its dissolution rate is several orders of magnitude smaller than even that of quartz[3].

3.1 In HF Solutions

The etch rate of silicon in the absence of an oxidant at room temperature at OCP is very low, on the order of 10^{-3} /s in concentrated HF solutions （ > 25% HF)[10]. It tends to decrease with immersion time. In HF-NH$_4$F solutions, the etch rate decreases with increasing HF at a constant NH$_4$F concentration and it increases with increasing NH$_4$F at constant HF concentration[11]. The etch rate of silicon in HF does not have a clear dependence on dopant concentration. Mechanistically, silicon dissolves mainly electrochemically in HF solutions in which participation of charge carriers is require[3]. At OCP the rate of dissolution is low because there are few carriers. The dissolution rate increases with potential to generate carriers at the surface as shown in Fig 4.

Addition of oxidants in HF solution can greatly increase etch rate. The most used oxidants for etching are HNO$_3$, Br$_2$, H$_2$O$_2$ and CrO$_3$. In particular, HF HNO$_3$ etching system is the most used isotropic etchant for silicon[12-13]. The mixtures of these two concentrated acids can be diluted with water or other dilutant to give a wide range of etch rates On the other hand, the HF-CrO$_3$ etching system is widely used for defect etching and delineation of junctions between silicon layers of different doping concentrations[14-15].

3.2 In Alkaline Solutions

The most commonly used alkaline solutions have been KOH and EDP (or EPW） which is a mixture of ethylenediamine (ED or E), pyrocatechol(P) and water (W)[16-17]. Other solutions such as NHOH$_4$, hadrazine, ethanolamine and tetramethyl ammonium

hydroxide（TMAH） are also used. The development and application of these etching solutions are dictated by a number of factors such as etch rate, anisotropic selectivity, corrosiveness to masking materials, surface quality, processing controllability, safety, and more recently environmental impact

Silicon etching in KOH solutions have been extensively investigated, resulting in a body of information that shapes the current understanding of the etching behavior of silicon in alkaline solutions. The major characteristics and the principle reaction processes involved in all alkaline solutions appear to be similar to that in the KOH system although the detail characteristics vary from system to system. Most notably, an alkaline solutions show the sensitivity of etch rate to crystal orientation, which is the basis for anisotropic etching Also, all these etchants show an etch rate reduction for highly boron doped materials The alkaline etchants can be made of organic and inorganic solutions, but all of them appear to require the presence of water to etch silicon at significant rates

The etch rate of silicon in KOH may vary from as low as 1   /s in dilute KOH (e. g   0. 5 mol/L） at room temperature to as high as 2 000   /s in a concentrated solution (e. g 40% KOH) at high temperatures For a given type and orientation the etch rate is essentially independent of doping concentration up to a concentration of about 10^{19} /cm^3[18-19]. At a doping level of about 2×10^{19} /cm^3 the etch rate of boron doped silicon drastically decreases with increasing dopant concentration, particularly for boron doped materials Thus, reduction by as much as three orders of magnitude can be obtained by varying the boron concentration from about 10^{19} /cm^3 to above 10^{20} / cm^3. This feature has been widely used as an etch-stop technique for the fabrication of silicon microstructures

The etch rate of all silicon materials in KOH depends, to a varying extent, on potential[20-22]. However, the contribution of electrochemical reactions, relative to chemical reactions, in etch rate is small Etch rate is the highest at OCP. At potentials positive of the passivation potential etching stops due to the

formation of an oxide film. At cathodic potentials, the effect is different for n-Si and p-Si. For n-Si etch rate decreases with increasing cathodic bias and etching stops at certain potentials. For p-Si the etching at cathodic potentials maintains relatively a high rate comparable to that at OCP.

3. 3   Anisotropic Dissolution

A characteristic feature of silicon etching in alkaline solutions is anisotropic etching, i e. , different dissolution rates on different crystal planes. Strictly speaking, the etch rate of silicon always depends, to a various extent, on crystal orientation in all etching solutions, acidic or alkaline. However, the etch rate difference among different planes is small in acidic HF solutions compared to those in alkaline solutions[23-29].

Anisotropic dissolution of crystal surface results in the formation of surface contour whose geometric features depend on the crystal orientation[27]. During steady state etching the etched surface profile exhibits a characteristic shape: convex or concave[30]. Etching of sphere, which is a convex surface, will result in a polyhedron hounded by faces, which exhibit high etch rates, and vertices corresponding to minima in etch rates. Since the fast etching planes vary with solution composition, the faces and vertices of etched polyhedron also vary. Using masks of different shapes and orientations and controlling the planes to disappear and develop during etching, various etched features such as cavity or pyramid can be obtained from anisotropic etching[31].

4   Surface Structures Resulted from Dissolution

The surface topography related to roughness is the roost basic surface microstructures that is resulted from the dissolution of silicon occurred in the various wet steps. Controlling these random microstructures to a minimal scale through polishing and cleaning, which is currently an active research area, is very important to the performance and reliability of advanced electronic devices[30-34].

Pits and groves resulted from etching are the sur-face structures related to the preferential dissolution associated with substrate defects. Defect etching is a simple and fast method to determine the structural perfection of single crystal. The morphological features developed by defect etching have a characteristic shape and may occur at random or in arrays revealing crystalline imperfections such as dislocation, slip, lineage, and stacking faults. Defect etching has been widely used to evaluate dislocations and also to delineate process-induced defects in silicon wafers and epitaxial deposits. Many different etchants, most of which are based on CrO_3 added HF solutions, have been developed for various purposes. By using proper etchants and procedures, different types of crystal defects can be evaluated.

Well-defined surface structures can be generated through etching to selectively remove materials from the surface. The important aspect of such etching process is the ability to control the amount of materials removed with sufficient spatial accuracy. The process and structural diversity in device fabrication necessitates diverse etching techniques, chemical or electrochemical, junction, anisotropicity, masking, and illumination to provide uniform and selective etching with lateral selectivity as well as in-depth selectivity.

The most fascinating structures found silicon electrodes are porous silicon formed by anodic dissolution in HF solutions. The morphology of porous silicon has an extremely rich details with respect to the range of variations in pore size, shape, orientation, branch, interconnection, and distribution[34-37]. Fig 6 shows the condition for occurrence of PS formation and electropolishing[6]. The three regions in relation to current density and HF concentration are essentially independent of the silicon substrate doping type and concentration, which means that the differences in semi-conducting properties of the silicon samples have little effect on the occurrence of these regions. The various parameters involved in PS formation such as potential, doping, and illumination, affect the occurrence of the different regions through their relation to the current density. Low current and high HF concentration favours PS formation while high

current and low HF concentration favours polishing

While the condition for PS is essentially independent of the condition of the silicon substrate, the morphology of PS, on the other hand, is strongly dependent on the factors related to the substrate. For example, doping concentration, which does not affect the nature of electrochemical reactions, is a principle factor in determining the morphology of porous silicon. Qualitatively, the diverse morphological features of FS reported in the literature can be summarised to six different aspects: pore shape, pore orientation, shape of a pore bottom, fill of macro pores, branching, and depth variation of a PS layer.
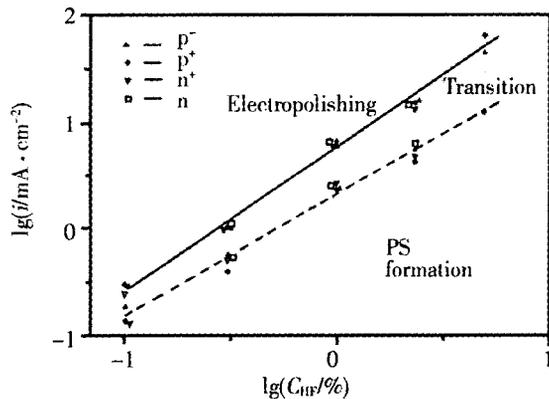
Fig 6   Occurrence of different regions as a function of HF concentration

The rich details of PS morphology are determined by the numerous factors involved in the anodization. Generally, p-Si and n-Si have distinct differences in the correlation between the formation conditions and PS morphology. Also, among all formation conditions doping concentration appears to show the most clear functional effect on morphology. As the most quantifiable parameter the diameter of pores appears, as a rough generalisation, to have certain qualitatively correlation with the various morphological aspects. More detailed description of the morphology of porous silicon and discussion of the formation mechanisms are documented in a recently published book: " Electrochemistry of Silicon and Its Oxide"[3].

References:

[1]   Kern W. [J]J. Electrochem. Soc. , 1990, 137: 1887.

[2]   Bassous E. Transactions on Electron Devices [M]. IEEE. 1978. Vol ED-25, 1178.

[3]   Zhang X G Electrochemistry of Silicon and Its Oxide [M]. Beijing: Chinese Chemical Industry Press, 2004.

[4]   Chazalvie J N. Etman 1M, Ozanam F[J]. J. Electroanal Chem. , 1991, 297: 533.

[5]   Chen L C, Chen M, Lien C et al [J]. J. Elechochem. Soc. , 1995,. 142:. 170.

[6]   Zhang X G, Collins S D, Smith R L. [M]. J. Electrochem. Soc. , 1989, 136:. 1561.

[7]   Memming R, Schwandt G. [J]. Surf. Sci. 1966, 4: 109.

[8]   Chazalviel J N, Etman M, Ozanam F[J]. J. Electroanal Chem. , 1991, 297: 533.

[9]   Palik E D, Glembocki O J, Heard I [J]. J. Electroche. Soc. , 1987, 134: 404.

[10]   Willeke G, Kellermann K [J]. Semicond Sci Technol , 1996: 11: 415.

[11]   Myamoto M, Kita N, Ishida S, et al [J]. J. Electrochem. Soc. , 1994, 141: 2899.

[12]   Ghandhi S K [M]. New York: in VLSI Fabrication Principles, John Willey & Sons, 1983.

[13]   Kooij E S, Butter K, Kelly J J. [J]. Electrochemical and Solid State Letter, 1999, 2: 178.

[14]   Wijaranakula W. [J]. J. Electrochem. Soc. , 1994, 141:. 3273.

[15]   Yang K H. [J]. J. Electrochem. Soc. , 1984, 131: 1140.

[16]   Seidel H, Csepregi L, Heuberger A et al [J]. J. Electrochem. Soc. , 1990, 13: 3612.

[17]   Van den Meerakker J E A. Van den Straaten M H M. [J]. J. Electrochem. Soc. , 1990. 137: 1239.

[18]   Seidel H, Csepregi L, Heuberger A, et al [J]. Ibid, Soc. , 1990, 137: 3626.

[19]   Palik E D, Faust J W, Gray Jr H F, et al [J]. Ibid , 1982, 129: 2052.

[20]   Glembocki O J, Stahlbush E, Tomkiewicz M. [J]. J. Electroche. Soc. , 1985, 132: 145.

[21]   Smith R L, Kloeck B, DeRooij N, et al [J]. J. Electroanalytical Chem. & Interfac. Electrochem. , 1987, 238: 103.

[22]   Bressers P M . M C, Pagano S A S P, Kelly J J. [J]. J. Electronanal Chem. , 1995, 391: 159.

[23]   Price J B. Semiconducotr Silicon [M]. Eds Huff H R, Burgess R R, Electrochem. Soc. : 1973. 339.

[24]   Seidel H, Csepregi L, Heuberger A, et al [J]. J. Electrochem. Soc. , 1990, 137: 3612

[25] Calabrese G S, W righton M S [J]. J. Electrochem. Soc. , 1981, 128: 1014.

[26] Sato K, Shikita M, Yamashiro T, et al [J]. Sensors and Actuators, 1999, 73: 131.

[27] Tellier C R, Brahim-Bounab A. [J]. Journal of Materials Science, 1994, 29: 5953.

[28] Zhang Q, Liu L, Li Z [J]. Sensors and Actuators A, 1996, 56:. 251.

[29] Hesketh P J, Ju C, Gowda S, et al [J]. Electrochem. Soc. , 1993, 140: 1080.

[30] Gatos H C, Lavine M C. [M]. Burgess: in Progress in Semicopnductors, Volume 9, eds A. F. Gibon and R. E. , CRC Press, 1965.

[31] Gorostiza P, Diaz R, Sanz F, et al [J]. J. Electro-

chem. Soc. , 1997, 144: 4119.

[32] Norga G J, Platero M, Black K A, et al [J]. J. Electrochem. Soc. , 1997, 144: 2801.

[33] Kloeck B, Collins S D, Rooij N F, et al Transactions on Electron Devices [M]. IEEE, 1989, 36(4): 6631

[34] Chen LC, Chen M, Tsaur T H, et al [J]. Sensors and Actuators A, 1995, 49: 115.

[35] Lehmann V, Stengl R, Luigart A. [J]. Materials Science and Engineering, 2000, 69: 11.

[36] Zhang X G [J]. J. Electrochem. Soc. , 1991, 138: 3750.

[37] Al Rifai M H, Christopherson M, Ottow S, et al [J]. Electrochem. Soc. , 2000, 147: 627

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