

SURFACE STRUCTURES AND SURFACE PROCESSES OF CERAMICS WITH ATOMIC RESOLUTION - A STUDY BY SCANNING TUNNELING MICROSCOPY

FINAL REPORT

IGNATIUS S.T. TSONG WILLIAM T. PETUSKEY

DECEMBER 10, 1991

U.S. ARMY RESEARCH OFFICE

CONTRACT NO. DAAL03-88-K-0098

ARIZONA STATE UNIVERSITY

APPROVED FOR PUBLIC RELEASE: DISTRIBUTION UNLIMITED.







MASIER COPY KEEP THIS COPY FOR REPRODUCTION PURPOSES

•}

*

.

REPORT DOCUMENTATION PAGE			Form Approved OMB No 0704-0188
Public reporting burden for this collection of i gathering and maintaining the data needed, a collection of information, including suggistion Davis Highway, Suite 1204, Arlington, v.A. 2220	nformation is estimated to average 1 hour per nd completing and reviewing the collection of i is for reducing this burgen. Ic Washington Hea 22-4302 and to the Office of Management and	response, including the time for rev nformation - Send comments regard dquarters Services, Directorate for Budget - Paperwork Reduction Project	rewing instructions, searching existing data sources sing this burden estimate or any other aspect of this information Oberations and Reports, 1215 Jefferson ct (0704-0188), Washington, DC 20503
1. AGENCY USE ONLY (Leave bla	nk) 2. REPORT DATE 10 December 1991	3. REPORT TYPE AND Final, 1 June	DATES COVERED 1988 - 30 September 1991
4. TITLE AND SUBTITLE			5. FUNDING NUMBERS
Surface structures a atomic resolution-a	nd surface processes o study by scanning tunr	f ceramics with eling microscopy	
6. AUTHOR(S)			
Ignatius S.T. Tsong William T. Petuskey			-
7. PERFORMING ORGANIZATION I	AME(S) AND ADDRESS(ES)		8. PERFORMING ORGANIZATION
Arizona State Univer Tempe, AZ 85287	rsity		REPORT NUMBER
9. SPONSORING / MONITORING AC	SENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING / MONITORING
U. S. Army Research	Office		AGENCY REPORT NUMBER
P. O. Box 12211			
Research friangle ra	rk, NC 27709-2211		
11. SUPPLEMENTARY NOTES			
The view, opinions a author(s) and should	and/or findings contain 1 not be construed as a	ned in this repor an official Depar	t are those of the tment of the Army
12a. DISTRIBUTION / AVAILABILITY	STATEMENT	lesignated by oth	12b. DISTRIBUTION CODE
Approved for public	release; distribution	unlimited.	
13. ABSTRACT (Maximum 200 wor We applied a new ter to study the atomic ar	ds) chnique for surface imag id electronic structures of	ging, scanning tunr ceramic surfaces.	neling microscopy (STM), The model ceramic
chosen for this study w	as SiC. STM imaging v render them semicondu	vas possible when t	resolved images were
successfully taken on s	urfaces of cubic β -SiC(10	(111), which wh	ch showed a variety of
reconstructions. In par	ticular, the STM images of	of the β -SiC(111) s	surface showed a 6 x 6
geometry, in contrast to	b a $6\sqrt{3} \times 6\sqrt{3}$ geometry	when measured by	y low-energy electron
incommensurately grow	n on top of the Si-term	inated B-SiC(111)	surface. This conclusion
was reached after pro	bing the electronic strue	cture of the surfa	ce by scanning tunneling
spectroscopy (STS). O	n a larger scale, i.e. over	distances between	50 nm and 500 nm, the
surface topographics of	oserved by STM were co	orrelated with the	initial growth modes of
theoretical investigation	ons on the thermochemic	istry and interfaci	al displacement reactions
of the Ti-Si-C and Ti	-Si-N systems in order to	o refine the unders	standing of thermodynamic
and phase equilibria	characteristics of cerami	c-metal composite	systems.
14. SUBJECT TERMS			15. NUMBER OF PAGES
			16. PRICE CODE
17: SECURITY CLASSIFICATION	18. SECURITY CLASSIFICATION	19. SECURITY CLASSIFIC	ATION 20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL
NSN 7540-01-280-5500			Standard Form 298 (Rev. 2-89)

TABLE OF CONTENTS

e

ډ

		U	
I.	Statement of the Problem	1	
II.	Summary of the Most Important Results	1	
	11.1 STM Studies of the β -SiC(100) Surface	1	
	II.2 STM Studies of the β -SiC(111) Surface	2	
	II.3 STM Studies of β -SiC(111) and α -SiC(0001)		
	Surfaces Under External Stresses	5	
	II.4 Physical Chemistry and Reaction		
	Chemistry of SiC Ceramics	5	
ш.	Publications List	8	
	III.1 Papers Published, In Press, and Submitted	8	
	III.2 Ph.D. Dissertations	9	
IV.	Participating Personnel		
V.	Inventions	9	
VI.	Figure Captions and Figures	10	

	Accession For				
	NTIS	GRALI			
	DTIC	TAB	ā		
	Unamounced				
	Justification				
	By				
	Distribution/ Availability Codes				
\frown					
	Avail and/or				
Contract y	Dist	Spec	ial		
3	1-0				
	1				

I. STATEMENT OF THE PROBLEM

,

Virtually all properties of a solid surface, whether they are physical, chemical, mechanical, or electrical, and all processes that take place on a surface, such as nucleation and growth of single crystals, and adhesion of thin films and coatings, ultimately relate to the atomic and electronic structures of that surface. The invention of the scanning tunneling microscope (STM) by Nobel laureates Gerd Binnig and Heinrich Rohrer has enabled scientists to obtain atomically-resolved images of a surface and by so doing, has completely revolutionized the study of surfaces. STM imaging, until a few years ago, was almost exclusively limited to surfaces of metals, semi-metals and semiconductors. Ceramic surfaces were largely ignored because it was thought that their non-conducting nature would preclude tunneling and imaging would therefore be impossible. We set out to solve the problem of using the STM to obtain atomically resolved images of a ceramic surface. We chose, as our model ceramic, SiC because of its important structural and electronic properties. Our goal was not limited to using the STM merely to obtain images of the surface atoms. We also intended to use the STM to perform spectroscopic measurements on the electronic structure of the surface, and to use the STM to investigate other fundamental problems such as the role of surface defects on the mechanical behavior of the surface under external stresses, the influence of different modes of film growth on the surface topography and its atomic geometry, and the surface reactions between a metal and a ceramic. The last of these problems has led us to conduct a separate experimental and theoretical investigation on the interfacial reactions of the Ti-Si-C system as a precursor to our intended STM study.

II. SUMMARY OF THE MOST IMPORTANT RESULTS

II.1. STM Studies of the β -SiC(100) Surface

The β -SiC(100) single crystals were grown on Si(100) substrates by chemical vapor deposition (CVD) and they were supplied by R. F. Davis of North Carolina State University. The β -SiC(100) surfaces were annealed at

high temperatures, i.e. between 1150 and 1200°C, in ultrahigh vacuum to eliminate the surface oxide prior to tunneling. The samples were nitrogendoped to a level of ~ 10^{16} cm⁻³ to render them n-type so that tunneling was not a problem.

The STM images showed that the β -SiC(100) surfaces were generally rough and uneven, with a corrugation of ~ 20 Å over 500 Å distances. We attribute the surface undulation to the lattice mismatch between the β -SiC(100) and the Si(100) substrate, i.e. 3.10 Å versus 3.84 Å. Despite the difficulty in obtaining atomically resolved images on such rough surfaces, we were able to observe ordered regions where c(2x2), (3x2) and other large reconstructions took place. Our results were reported in detail in paper #5 on our publication list.

II.2. STM Studies of the β -SiC(111) Surface

The β -SiC(111) single crystals were grown on hexagonal α -SiC(0001) substrates by CVD and they were also supplied by R. F. Davis of NCSU. Two types of β -SiC(111) surfaces were available, one was grown on the Siterminated α -SiC(0001) surface while the other was grown on the Cterminated α -SiC(0001) surface. Large scale STM scans showed that the latter was considerably less smooth and contained numerous doublepositioning boundaries separating domains with different stacking order. This observation suggests that the lateral epitaxial growth of the β -SiC film on the C-terminated α -SiC(0001) surface is restricted by the greater activity and higher sticking coefficient on the C-face. As a result, the mobility of the atoms on the surface is decreased and vertical growth dominates. Atomic resolution imaging was not possible on the β -SiC(111) grown on the C-terminated α -SiC(0001) surface because the corrugations on the domains were greater than the atomic corrugation. These results are discussed in detail in paper #6 on our publication list.

STM imaging with atomic resolution was easily achieved on the β -SiC(111) surface grown on the Si-terminated α -SiC(0001) substrate face. Fig. 1 shows voltage-dependent scans of the same region on a β -SiC(111) surface after a 1200°C annealing treatment to rid the surface of oxides.

The surface shows a 6 x 6 geometry with a unit-cell edge of ~19 Å, which is approximately six times the unit-cell edge of 3.1 Å of the β -

SiC(111)-(1x1) bulk-terminated surface. The images (a) and (b) of Fig. 1 were taken simultaneously on the same area with the tip biased at +3.7Vwhen scanning from left to right and biased at -3.7V when scanning from right to left. The most remarkable feature in these two scans is the occurrence of a contrast reversal. The honeycomb pattern in the filledstate image (a) turns into a centered-hexagon array in the empty-state image (b). The minima of the honeycombs in (a) coincide exactly with the maxima of the centered-hexagons in (b). Each honeycomb minimum and each hexagon maximum has a diameter of ~12 Å, clearly much larger than the size of a single atom. The corrugation of both images was about 0.4 Å.

.

The spectroscopy of the surface was performed by measuring current-voltage (I-V) dependence under the condition of constant tipsample separation. This was achieved by holding the voltage on the feedback loop constant for about 150 ms during the acquisition of an I-V curve. Generally, ten I-V curves were collected at the same tip-sample gap and their average taken to give the I-V curve for that gap. From the averaged I-V curves, we plotted (dI/dV)/(I/V) or (dlnI/dlnV) versus V or energy, which has been shown to represent features of the surface density of states (DOS). Fig. 2 shows such a (dI/dV)/(I/V) versus energy curve, giving spectroscopic information of the surface.

Interestingly, our LEED studies of the β -SiC(111) surface annealed at 1200°C showed a $6\sqrt{3} \times 6\sqrt{3}$ geometry, in agreement with previous LEED experiments by other workers taken on an equivalent α -SiC(0001) surface. The 6 x 6 geometry in STM images was not observed by LEED.

In order to explain why the STM gives a 6 x 6 geometry of the β -SiC(111) surface whereas the LEED gives a $6\sqrt{3} \times 6\sqrt{3}$ geometry for the same surface, we invoke a model originally proposed by van Bommel and coworkers at Philips Research Laboratories for their LEED studies of the α -SiC(0001) surface. Three successive carbon layers of β -SiC, after the evaporation of silicon by annealing to 1200°C, collapse into one single layer of carbon atoms with a surface density of 3.67 x 10¹⁵ atoms cm⁻², very close to the density of a graphite monolayer of 3.80 x 10¹⁵ atoms cm⁻². This layer of carbon atoms then have only to be displaced over small distances to form a graphite layer. Support for the existence of the graphite monolayer can be found in the tunneling spectrum shown in Fig. 2, where peaks at -2.6, 1.3 and 2.5 eV agree with the -2.5 eV π -bonding

state, 1.3 eV π^* -antibonding state, and the 2.5 eV surface state in the surface electronic spectra of graphite calculated theoretically.

In Fig. 3, we have drawn a graphite mesh with periodicity (or unitcell edge) of 2.46 Å over a Si bulk-terminated (1x1) surface of β -SiC(111) with periodicity of 3.1 Å. The positions where the top C utoms coincide exactly with the Si atoms underneath are marked with circles and labeled A, B, C, D, E and F. These positions give rise to the $6\sqrt{3} \times 6\sqrt{3}$ geometry observed by LEED since the unit-cell edges, AE and CE, each has a length of 13 graphite hexagons, i.e. 13 x 2.46 Å, which is virtually identical to $6\sqrt{3}$ times 3.1 Å. Around each of the positions A-F, there are three pairs of C and Si atoms at the apexes of the dotted triangle lying very close to each other, i.e. within 0.3 Å laterally. The position G, given by the dotted circle in Fig. 3, does not have any C atoms directly above a Si atoms. Six C atoms on the dotted circle, however, are lying very close to six Si atoms. ABGF forms the 6x6 geometry observed by STM. To explain the contrast reversal phenomenon as the tip bias is reversed, we need a detailed knowledge of the electronic structure of the surface.

We have performed first-principles calculations of the electronic structure of the surface shown in Fig. 3. Our calculations, which explain the contrast reversal phenomenon, are summarized in Fig. 4 which shows the partial density of states for the graphite monolayer and those for the Si-terminated surface of β -SiC(111) underneath. Since the work function for the graphite monolayer is smaller than that for the Si-terminated β -SiC(111), there is a net charge transfer from the graphite to the β -SiC. The graphite Fermi level is located at the π band, which is composed solely of P_z orbitals; here z is the coordinate normal to the surface. When there is a Si atom directly beneath or close to a C atom in the graphite layer, i.e. positions A-G in Fig. 3, the charge transfer occurring between these atoms will be maximum, resulting in the increase of the number of empty states of the C atoms. So when the empty states are probed by the negativelybiased tip, the positions A-G appear bright, forming a centered hexagon pattern as in Fig. 1(b). When the tip is biased positively and sampling the filled states, positions A-G appear dark because of the depletion of filled states due to the charge-transfer from the tilled states of the C atoms to the Si dangling-bond states underneath. This results in the honeycomb

pattern in Fig. 1(a). Thus the voltage-dependent contrast reversal is explained.

\$

1

We conclude that the discrepancy between the 6 x 6 STM geometry and the $6\sqrt{3} \times 6\sqrt{3}$ LEED pattern for the β -SiC(111) surface can be explained by an incommensurate graphite monolayer grown on the Si-terminated β -SiC(111) surface during the annealing process. The contrast reversal phenomenon observed in the STM images at opposite tip biases can be explained by the different electronic contributions from graphite states of those C atoms with Si atoms directly (or almost directly) underneath and those without. The details of our results can be found in papers #7 and #8 in our publication list.

II.3 STM Studies of β -SiC(111) and α -SiC(0001) Surfaces Under External Stresses

An STM with a strain stage was specially built to conduct experiments in which a SiC cample was subjected to an external stress. The sample consisted of a long thin SiC single crystalline wafer clamped at one end. The other free end could be pushed or pulled by small amounts adjusted via a UHV rotary-linear feedthrough. The single crystalline β -SiC(111) and α -SiC(0001) wafer were supplied by Cree Research in North Carolina. Since the application of stress could be finely adjusted, we hoped to observe the initiation of cracking and fracture on an atomic scale on the surface, and the role played by vacancies, dislocations and steps in such a process. Success of the experiment, however, was limited up to the termination date of this project. There were numerous problems in this very delicate experiment and we were just beginning to overcome them. We have no doubt that we will succeed, but we need more time.

II.4 Physical Chemistry and Reaction Chemistry of SiC Ceramics

The thrust of this project from the materials science perspective has been to examine important issues concerning the physical chemistry of silicon carbide-metal alloys and composites. The reason is that the application of silicon carbide as a structural material will likely be in the form of a composite. Consequently, the specific issues that we are

addressing concern the chemical and mechanical compatibility of silicon carbide with the other components. This necessarily involves a detailed examination of interface compatibilities and reactions.

We have focused our investigation principally on the Si-Ti-C system since SiC-TiC and SiC-Ti composites hold some promise as high strengthhigh toughness materials. To a lesser extent, we have studied SiC based composites based on the Si-Al-C-N system. This is of interest due to the capability of forming finely dispersed spinodal-like phase distributions of SiC and AlN, which ultimately contains features desirable for high toughness ceramics.

We undertook a detailed evaluation of the thermochemistry of the Ti-Si-C and Ti-Si-N nitrogen systems by combining reliable information from the literature with our own experimental work directed at clarifying a number of the outstanding inconsistencies existing up to present. We revised the ternary phase diagrams for these systems providing more detail concerning the binary and ternary phase equilibria. However, what was most novel about our work was the construction of the phase stability diagrams and demonstrating how they might be used for interpreting complex series of reactions often seen at reaction interfaces. A stability diagram maps out the stability criteria for each phase of a system in terms of chemical potential (partial molar free energy) and composition space. On this diagram, the reaction paths taken at an interface can be traced allowing a rational analysis of the sequence phases formed. Successive analyses as a function of time and temperature provides sufficient information to provide some predictive power in controlling the reactions.

An example appears in Fig. 5 corresponding to the Ti-Si-C system. The chemical potential of silicon (or rather the activity of silicon where log $a_{Si} = \mu_{Si}/2.303$ RT) is plotted as function relative fraction of titanium and silicon. The shaded regions correspond to solid solution phases of significant range of stoichiometry. Horizontal lines represent three phase equilibria and the open fields represent two phase equilibria. The reaction between Ti metal and silicon carbide are followed for two different cases corresponding to different times of reaction. Case II corresponds to relatively short reaction times where at one extreme of no titanium, silicon carbide is stable for log $a_{Si} > 2.0$ and titanium metal is stable at the other extreme at much lower silicon activities. The reaction paths show

intermediate phases of TiC_x and $Ti_5Si_3C_v$ which appear as combinations of layered and mixed phase morphologies. At longer times (Case I), the ternary compound Ti₃SiC₂ appears as a continuous layer adjacent to silicon carbide. This comparison points out that the reaction can be thought of as a dual problem of interdiffusion of Ti with Si and Ti with C. Because carbon diffuses much more rapidly in general than silicon, the reaction zone is gradually but continuously depleted of carbon, thus enriching itself in silicon which is left behind. An increasing silicon activity destabilizes TiC next to silicon carbide to favor the formation of the ternary compound. A continuation of this trend would predict that eventually the silicide phase TiSi₂ would form, which is undesirable because of brittleness and poor bonding characteristics. This is indeed what has been found for composite and thin interfaces which have been overannealed. It is interesting to note that the effect of annealing temperature is very similar to that of annealing time, i.e. increasing temperature tends to raise the relative silicon content in the reaction.

2

We investigated the phase relationships of these reactions (Ti-Si-C $_{2}$ ystem) at pressures up to 20 kbar. Our study was used to demonstrate the effect of nonuniform stresses on phase sequences and morphologies at reaction interfaces. Composites of unusual geometries, or ill-controlled geometries, can give rise to local stresses and stress gradients due to mismatch of thermal expansion coefficients. It was shown for reaction conditions at 1200°C that local compressive stresses could exceed a threshold defining different compatibility relationships phases. For example, high pressures tended to stabilize the phase Ti₃Si which, like other silicides, was undesirable for its bonding characteristics.

Details of this investigation appear in papers #9 and #10 in our publication list.

III. PUBLICATIONS LIST

à

:

III.1. Papers published, in press, and submitted.

- Z.J. Zheng, I.H. Wilson, U. Knipping, D.M. Burt, D.H. Krinsley and I.S.T. Tsong. Atomically Resolved Scanning Tunneling Microscopy Images of Dislocations. Phys. Rev. <u>B38</u>, 12780-12782 (1988).
- I.H. Wilson, N.J. Zheng, U. Knipping and I.S.T. Tsong. Scanning Tunneling Microscopy of an Ion-Bombarded PbS (001) Surface. Appl. Phys. Lett. <u>53</u>, 2039-2041 (1988).
- I.H. Wilson, N.J. Zheng, U. Knipping and I.S.T. Tsong. Scanning Tunneling Microscopy of Ion Impacts on Semiconductor Surfaces. J. Vac. Sci. Technol. <u>A7</u>, 2840-2844 (1989).
- 4. N.J. Zheng and I.S.T. Tsong. Resonant Tunneling Theory of Imaging Close-packed Metal Surfaces by Scanning Tunneling Microscopy. Phys. Rev. B <u>41</u>, 2671-2677 (1990).
- 5. C.S. Chang, N.J. Zheng, I.S.T. Tsong, Y.C. Wang and R.F. Davis. Scanning Tunneling Microscopy of Cubic Silicon Carbide Surfaces. J. Am. Ceram. Soc. <u>73</u>, 3264-3268 (1990).
- C.S. Chang, N.J. Zheng, I.S.T. Tsong, Y.C. Wang and R.F. Davis. Studies of β-SiC(001) and (111) Surfaces by Scanning Tunneling Microscopy. J. Vac. Sci. Technol. <u>B9</u>, 681-684 (1991).
- C.S. Chang, I.S.T. Tsong, Y.C. Wang and R.F. Davis. Scanning Tunneling Microscopy and Spectroscopy of Cubic β-SiC(111) Surfaces. Surface Sci. <u>256</u>, 354-360 (1991).
- M.H. Tsai, C.S. Chang, J.D. Dow and I.S.T. Tsong. Electronic Contributions to Scanning Tunneling Microscopy Images of an Annealed β-SiC(111) Surface. Phys. Rev. B (in press).
- 9. S. Sambasivan and W.T. Petuskey. Thermodynamics of Forming Ti₃SiC₂. J. Am. Ceram. Soc. (submitted).
- 10. S. Sambasivan and W.T. Petuskey. Phase Relationships in the Ti-Si-C System at High Pressures. J. Mater. Res. (submitted).

 S. Sambasivan and W.T. Petuskey. Thermochemical Interpretation of Solid State Reactions in the Ti-Si-N System, I. Phase Stability. J. Mater. Res. (submitted).

III.2. Ph.D. Dissertations

3

- Jason R. Guth Theoretical and Experimental Studies of Silicon Carbide Polytypes and Solid Solution Crystal Structures
- 2. Nanjiu Zheng Scanning Tunneling Microscopy
- 3. Sankar Sambasivan Thermochemistry of Ceramic-Metal Reactions in Ti-Si-N and Ti-Si-C Systems at High Temperatures and Pressures

IV. PARTICIPATING PERSONNEL

I.S.T. Tsong - Principal Investigator
W.T. Petuskey - Co-principal Investigator
C.S. Chang - Postdoctoral Research Associate
J.R. Guth - Graduate Assistant - Ph.D. (1989)
N.J. Zheng - Graduate Assistant - Ph.D. (1990)
S. Sambasivan - Graduate Assistant - Ph.D. (1990)
C.J. Kuo - Graduate Assistant
B.E. Steele - Graduate Assistant
J.L. Stevens - Graduate Assistant

V. INVENTIONS

None

VI. FIGURE CAPTIONS AND FIGURES

- Fig. 1 (a) 500 Å x 500 Å filled-state image of the β-SiC(111) surface.
 V_t = 3.7 V.
 (b) 500 Å x 500 Å empty-state image taken simultaneously of the same area as in (a). V_t = -3.7 V.
- Fig. 2 A tunneling spectrum, (dI/dV)/(I/V) as a function of energy, of the β -SiC(111) surface. Arrows indicate states associated with graphite.
- Fig. 3 A model of a graphite monolayer (represented by honeycombs) incommensurately grown on the (1x1) Si-terminated β -SiC(111) surface (represented by dots). The dashed triangles, denoted by A, B, C, D, E and F, indicate positions where the graphite atoms at the centers of triangles coincide exactly with the Si atoms in the second layer, and those graphite atoms at the apexes almost coincide with the Si atoms underneath. The dashed circle, G, outlines positions where the graphite and Si atoms nearly coincide. The unit cell spacing is 2.46 Å for graphite and 3.1 Å for the (1x1) Si-terminated surface.
- Fig. 4 Calculated partial density of states for the Si-terminated surface of β -SiC(111) and for the incommensurately grown graphite monolayer. The Fermi levels with respect to each other are shown below the vacuum level.
- Fig. 5 Phase stability diagram for Ti-Si-C system at 1200°C plotting the activity of silicon as a function of the relative concentration of titanium and carbon. The path of compositions and sequence of phases appearing in the reaction zone of Ti-SiC couples are plotted for two different cases. The annealling time for Case I was longer than for Case II.



(b)

(a)



3

۲

-



.



¥



Fig. 5