**Электротехника. Текст 1.**

Formation of a Buffer Layer for Graphene on C-Face SiC {0001}

Graphene films prepared by heating the SiCр000\_1Ю surface (the C-face of the

{0001} surface) in a Si-rich environment have been studied using low-energy

electron diffraction (LEED) and low-energy electron microscopy. Upon

graphitization, an interface with symmetry is observed

by in situ LEED. After oxidation, the interface displays

symmetry. Electron reflectivity measurements indicate that these interface

structures arise from a graphene-like ‘‘buffer layer’’ that forms between the

graphene and the SiC, similar to that observed on Si-face SiC. From a

dynamical LEED structure calculation for the oxidized C-face surface, it is

found to consist of a graphene layer sitting on top of a silicate (Si2O3) layer,

with the silicate layer having the well-known structure as previously studied

on bare SiCр000\_1Ю surfaces. Based on this result, the structure of the interface

prior to oxidation is discussed.

Key words: Thermal conductivity, thermoelectrics, interface, layered oxides,

molecular dynamics, phonon, cobaltite

INTRODUCTION

Graphene, a single sheet of sp2-bonded carbon

arranged in a honeycomb lattice, has potential for

use in novel electronic devices due to its unusual

electronic properties.1–3 Formation of graphene on

SiC has been intensively studied for the past several

years, since graphene formed in that way can have

large areas suitable for device and circuit fabrication.

3 There are two inequivalent faces of SiC{0001}:

the (0001) face, which is known as the Si-face, and

the р000\_1Ю face, known as the C-face. On both of

these surfaces, on heating to temperatures of about

1200\_C, Si atoms preferentially sublimate from the

surface, leaving behind excess C atoms that selfassemble

into graphene. On the Si-face, a number of

groups have succeeded in forming single-layer

graphene, with good reproducibility between

groups.3–6 In contrast, for the C-face, a number of

studies have revealed the formation of islands of

graphene instead of a uniform single layer.7–9

For graphene on SiC, it has been demonstrated

that new graphene layers are formed not on top of

existing ones but rather at the interfacebetween

existing graphene layers and the underlying substrate.

10 Hence, the starting surface of SiC and the

later interface structure between the graphene film

and the SiC substrate play a crucial role for subsequent

graphene formation. The graphene–SiC

interface is now quite well understood for the

Si-face: the interface consists of a C-rich layer having

symmetry (denoted 6for short), which is covalently bonded to the underlying

SiC substrate.10,11 This interface on the Si-face acts

as an electronic ‘‘buffer’’ layer between the graphene

films and SiC substrate and provides a template for

subsequent graphene formation.12 Here, by the

term ‘‘buffer layer,’’ we mean a layer that has nearly

the same structure as graphene, but is covalently

bonded to the underlying material and therefore has

different electronic structure than graphene.12 This

Si-face buffer layer has been observed by several

groups from samples prepared under various

conditions.3

**Электротехника. Текст 2.**

In our prior work, we prepared graphene on the

C-face of SiC in Si-rich environments, utilizing either

disilane at pressure of \_10\_4 Torr or cryogenically

purified neon at 1-atm pressure. We find that, when

graphene is prepared in these conditions, a new

interface structure with symmetry

is produced.14–16 After subsequent oxidation of

the surface by mild heating in the presence of oxygen,

the structure transforms to one with

symmetry. We have previously argued that both the

structures are indicative of a graphene-like buffer layer

that terminates the SiC crystal;15,16 That is, with

additional graphene formation on the surface, this

buffer layer is present at the interface between the

graphene and the SiC, just as occurs for the Si-face

surface.

In this work, we discuss the formation and

structure of the C-face buffer layer, providing new

results to illustrate its characteristics. First, we

summarize prior results for LEED patterns and

low-energy electron reflectivity (LEER) spectra of

the buffer layer. Both types of data were presented

in our prior work, but a complete understanding of

the LEER spectra in particular was not available at

that time. We subsequently developed a first-principles

method for computing such spectra,17,18 and

based on that we can now provide a more rigorous

interpretation of those spectra. Following that

 presentation, we then describe a

quantitative LEED structure determination for the

observed surface (i.e., the C-face buffer following

oxidation), revealing that its structure consists of a

graphene layer on top of a Si2O3 silicate layer.

Based on that result, we discuss the structure of the

C-face buffer layer prior to the oxidation.

This paper is organized as follows. In ‘‘Experimental

and Theoretical Methods’’ section, we present

details of our experimental and computational

methods. ‘‘Structural Models, LEED Patterns, and

LEER Spectra’’ section describes our results from

experimental LEED and LEER observations,

including presentation of structural models and definition

of the notation we use to refer to specific

layers of the structures.

**Электротехника. Текст 3.**

**EXPERIMENTAL AND THEORETICAL**

**METHODS**

Experiments were performed on nominally

on-axis, n-type 6H-SiC or semi-insulating 4H-SiC

wafers purchased form Cree Corp., with no apparent

differences between results for the two types of

wafer. The wafers were cut into 1 cm 9 1 cm samples.

To remove polishing damage, the samples were

heated in either 1 atm of hydrogen at 1600\_C for

3 min or 5 9 10\_5 Torr of disilane at 850\_C for

5 min. In the same chamber, graphene was formed

by heating in 5 9 10\_5 Torr of disilane. Characterization

by LEED was performed in situ in a connected

ultrahigh-vacuum (UHV) chamber.

For quantitative LEED analysis, diffraction spot

intensities were measured at different energies in

the range of 100 eV to 300 eV. For the SiC surface of

specific termination, a single domain with only one

orientation would give rise to a threefold-symmetric

LEED pattern in which the (10) and (01) spots have

different intensity spectra. Since sixfold-symmetric

LEED patterns were in fact observed, both possible

domains with different orientations, i.e., rotated by

60\_ with respect to each other, are present on the

surface. Spot intensities from two rotational domains

were averaged, and the resulting I(E) spectra were

compared with theoretical LEED calculations to

retrieve details of the atomic arrangement of the

interface structure. The theoretical I(E) was calculated

by full dynamical LEED calculations, and

optimization was carried out by tensor LEED, using

the calculation package from Blum et al.20 The

Pendry R-factor, Rp,21 was used for comparison

between experimental and calculated I(E) spectra.

**RESULTS**

**Structural Models, LEED Patterns, and LEER**

**Spectra**

Figure 1 shows structural models for the two surfaces

that are the topic of this paper: a graphene-like

buffer layer on C-face SiC, and the same buffer layer

on a surface which has been oxidized. In both figures,

the buffer layer is the topmost layer of the surfaces,

with a carbon atom density.

**Электротехника. Текст 4.**

The term ‘‘buffer layer,’’ which

we denote as ‘‘B,’’ is used in Fig. 1a to refer to this

graphene-like layer since it bonds to the underlying

SiC structure. Actually, the precise interface structure

between the graphene and the SiC is not known,

as indicated by the box with question marks in

Fig. 1a. However, what is known is that the nature

of the bonding between the buffer layer and the

underlying SiC changes as a result of oxidation of the

surface. As shown in Fig. 1b, we find that after oxidation

the SiC is terminated by a Si2O3 silicate and

the buffer layer above that silicate is only weakly

bonded to it. Hence, the buffer layer is decoupled

from the underlying structure (analogously to what

occurs on graphitized Si-face SiC22–25), and it forms a

regular graphene layer which we refer to as G0 (with

the subscript ‘‘0’’ referring to the fact that it originates

from the buffer layer).

The model shown in Fig. 1b is actually the result of

the detailed ‘‘LEED I–V Analysis’’ section, but we

introduce ithere in advance of that analysis in order to

provide some definiteness to the structures that we

discuss. Figure 2a and b show LEED patterns

acquired from the two surfaces corresponding to

Fig. 1a and b, respectively. The pattern in Fig. 2awas

obtained from a surface in situ immediately after

graphene preparation, which is done by heating the

sample in 5 9 10\_5 Torr of disilane at 1250\_C for

5 min. Weak graphene streaks and a complex

arrangement of spots are observed. As illustrated in

our prior work,15 the complex pattern can be indexed

using a supercellwith edges extending along (6,1) and

(\_1,7) of the SiC1 9 1 cells.Usingacompactnotation

we denote this structure as (denoted by

for short). After this in situ study, the

sample was exposed to air during transfer between

preparation and characterization chambers, and after

introduction into the low-energy electron microscopy

(LEEM) chamber itwas outgassed at about 1000\_C for

several minutes. This procedure caused the

pattern to disappear and a pattern to

appear, as showninFig. 2b.The same

pattern was found on samples that were exposed to

1 9 10\_5 Torr of pure oxygen (rather than air) while

heating to 1000\_C. So, the

pattern is an indication of oxidation of the surface, as confirmed

by the calculation in the following section.

**Электротехника. Текст 5.**

However,

from low-energy electron microscopy (LEEM) studies,

we know that, for any given 0.1 mm 9 0.1 mm

area of the sample within this center region, the

graphene coverage on the surface varies. For an

unoxidized sample, we observe the bare buffer layer

(B) together with areas of buffer layer plus graphene

(B + G) and occasionally buffer layer plus more

graphene layers (B + 2G or B + 4G). Similarly,

for an oxidized sample, we observe areas of decoupled

buffer layer which corresponds to a single

graphene layer (G0), together with areas of graphene

on top of that (G0 + G) or areas with additional

graphene layers. Most importantly, using LEEM,

we have performed spatially resolved diffraction

(l-LEED) at many individual micrometer-sized

locations over the center region of the samples. For

samples displaying LEED patterns such as those

shown in Fig. 2, i.e., with well-developed spots

prior to oxidation, we find that all such locations

display distinct graphene diffraction spots, arising

either from the coupled or decoupled buffer layer or

from graphene layer(s) on top of that. In addition to

graphene diffraction spots, some locations also display

the\_ pattern as seen in Fig. 3c

of our previous work.15 This coexistence of both

graphene and

 spots again confirms that a well ordered

oxidation layer forms underneath the

decoupled buffer layer.

LEER spectra measured by LEEM provide a

useful means of further characterizing the various

layers on the sample surface. Figure 3 shows

examples of such spectra, acquired from both

unoxidized and oxidized samples.16 These spectra of

Fig. 3 can be easily interpreted if we bear in mind

the recent interpretation that the minima in the spectra

arise from electronic states localized

between the graphene layers or between the bottommost

layer and the substrate.17,18 For n graphene

layers there are n \_ 1 spaces between them

and, hence, n \_ 1 interlayer states. An additional

state forms between the bottommost graphene layer

and the substrate so long as the space between those

is sufficiently large. Coupling (in a tight-binding

sense) between all the interlayer states then produces

a set of coupled states, and reflectivity minima

are observed at the energies of these coupled

states.