SiC nanocrystals on Si

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Introduction

SiC-based semiconductor electronic devices and circuits have great potential in the field of high-temperature, high power, high frequency and radiation-resistant applications, where conventional Si based semiconductors cannot adequately perform [1].

SiC has excellent mechanical properties (hardness, Young's modulus) and wear resistance, which makes it a desirable material for harsh environment MEMS (Microelectromechanical Systems) applications [2].

PECVD SiC thin film can be utilized not only as the structural material of MEMS devices, but also as a protective material for coating and packaging of micromachined Si parts [3].

Bulk SiC has indirect bandgap, however due to quantum confinement nanocrystalline SiC is capable of photoluminescence. Highly luminescent, biocompatible, hydrophilic SiC NC colloidal solution can be applied for tagging cells or molecules [4].

A unique method was developed in order to form SiC NCs at the Si side of a SiO_2/Si interface by CO annealing. The phenomena was discovered in 2002 by Krafcsik et al. and patented by the Department of Atomic Physics of the Technical University of Budapest and the Research Institute of Technical Physics and Materials Science [5–7].

Goals

Our group has previously shown that CO annealing of a SiO_2/Si structure at temperatures above 1000°C results epitaxial, void-free 3C-SiC nanocrystals at the Si side of the SiO_2/Si interface [5, 8].

From the application point of view we can define two different goals. For memory applications or for the strong room temperature photoluminescence due to quantum

confinement NCs with 2-3 nm size and with the highest possible nucleation density are desirable. Harsh environment MEMS applications need a flexible technology to form a continuous protective polycrystalline SiC coating with the lowest thermal budget.

The aim of this dissertation is to characterize and understand SiC NC formation mechanism at the SiO_2/Si interface made by annealing in CO. CO diffusion in SiO_2, nucleation and growth mechanism of SiC NCs has been studied by isotope tracing and various kinds of microscopy. Effect of process parameters on nucleation density, size and morphology has been investigated, such as CO pressure, annealing time, initial oxide thickness and orientation of the Si substrate. Electrical characterization of MOS structures with embedded SiC NCs has been carried out to identify the effect of CO annealing on electrical parameters.

Experimental methods

In order to monitor the atomic movement of carbon and oxygen during SiC NC growth SiO_2/Si structures were heat treated in isotopically labeled $^{13}C^{18}O$ gas at different pressures at 1100°C. This allowed us to investigate CO diffusion and SiC formation separately from ^{12}C and ^{16}O coming from the surface contamination and the bulk SiO_2. Depth profiles of ^{13}C and ^{18}O isotopes were taken by SIMS (Secondary Ion Mass Spectrometry) and NRA (Nuclear Reaction Analysis).

After performing heat treatments with different process parameters (CO pressure, annealing time, dielectric thickness, Si substrate orientation), nucleation, growth and morphology of the SiC NCs has been studied by SEM (Scanning Electron Microscopy), TEM (Transmission Electron Microscopy) and AFM (Atomic Force Microscopy).

Effect of CO annealing on electrical parameters of the SiO_2/Si structure and charge storage capability of SiC NCs has been investigated by current-voltage and capacitance-voltage measurements.

Theses

The major conclusions of my Ph.D. work are summarized in the following thesis points.

1. I found for the formation mechanism of SiC nanocrystals (NCs) in isotopically labeled $^{13}C^{18}O$ [T1,T2], that

(a) ^{13}C and ^{18}O accumulates at the SiO_2/Si interface at 1100°C. The amount of ^{13}C is proportional to CO gas pressure and the annealing time. These results are proved experimentally by isotopic tracing using SIMS and NRA.

(b) Applying the Deal-Groove theory to the diffusion and reaction processes of CO molecules in SiO_2/Si, I calculated the parabolic and linear constants ($k_p = 3.9 \pm 1.0 \times 10^{-16}$ cm$^2/s$ and $k_l = 1.3 \pm 0.2 \times 10^{-11}$ cm/s) and estimated the CO diffusion coefficient in amorphous silica at 1100°C ($D_{CO} = 1.8 \times 10^{-9}$ cm$^2/s$).

(c) SiC NC growth is not possible at the Si_3N_4/Si interface as Si_3N_4 is a diffusion barrier against CO, therefore selective growth of SiC NCs can be achieved by masking Si by Si_3N_4.

2. I found that for nucleation and growth of SiC NCs in 5×10^3 Pa (5 at.%) and 10^5 Pa (100 at.%) CO [T3,T10]

(a) nucleation density of SiC NCs increases with CO concentration (from 4×10^9 cm^{-2} to 4×10^{10} cm^{-2} by increasing the CO concentration from 5×10^3 Pa (5 at.%) to 10^5 Pa (100 at.%)) and CO pressure. Annealing a SiO_2/Si structure in 10^5 Pa (100 at.%) CO at 1100°C for 6 hours results a continuous polycrystalline SiC layer.

(b) lateral dimension of SiC NC is proportional to the square root of time based on microscopy studies. This implies that lateral growth is limited by diffusion and the carbon diffusion in Si might be the limiting process.

(c) grain boundaries and cracks in single crystal Si act as heterogeneous nucleation zones, with depleted, nucleation free zones around them (200-400 nm in 5×10^3 Pa (5 at.%) CO 1190°C, 30-50 nm in 10^5 Pa (100 at.%) CO 1100°C).

(d) I proposed a nucleation model, which can explain the pre-nucleation time, the relatively large size of the critical nucleus, the increasing nucleation density and decreasing critical nucleus size with increasing CO pressure.

3. I demonstrated experimentally that nucleation density, size and morphology strongly depends on the orientation of the Si substrate in 5×10^3 Pa (5 at.%) CO [T5,T6,T7, T8,T11].

(a) The SiC nucleation density on (110) is four times higher than on (100) and (111) surfaces. Nucleation density is not proportional to the Si/SiO_2 available bond density or interface state density. The smallest crystal size was obtained on the (110) plane. According to my experiments SiC formed on the (110) surface has the lowest formation energy resulting the smallest critical nucleation size and higher nucleation density.

(b) I proposed that morphology of nc-SiC was governed by crystal symmetry and elastic stress. Fourfold, rectangular and hexagonal symmetry of the Si substrate defines the shape on (100), (110) and (111) surfaces respectively. Convex equilibrium shapes on (100) and (111) surfaces suggest that elastic energy contribution is remarkable in the shape definition.

4. I found for the electrical parameters of MOS structures with SiC NCs [T4,T9], that

(a) CO annealing does not affect the insulating properties of the SiO_2 layer according to C-V measurements.

(b) negative flatband shift appears up to several volts after CO annealing by C-V measurements caused most likely by positively charged oxygen vacancies in the SiO_2, which I successfully eliminated by a post-oxidation treatment.

(c) it is possible to inject carriers into the SiO_2 isolated SiC NCs in the dielectric layer of MOS structures created by post-oxidation step. The number of the injected carriers is in the 10^{10}-10^{11} cm^{-2} range, the hysteresis window in the samples is 0.22-0.67 V and can be tuned by the process parameters.

Publications referred in my thesis points:

Journal papers:

[T1] **Isotopic tracing study of the growth of silicon carbide nano-crystals at the SiO_2/Si interface by CO annealing**
A. Pongracz, Y. Hoshino, M. D'Angelo, C. Deville Cavellin, J.-J. Gange, I. Trimaille., G. Battistig, K.V.Josepovits, I. Vickridge
J. Appl. Phys. Vol. 106 **(2009)**, 024302

[T2] **An ^{18}O study of the interaction between carbon monoxide and dry thermal SiO_2 at 1100°C C.**
D. Cavellin, I. Trimaille, J. J. Gange, M. D'Angelo, I. Vickridge and A. Pongracz, G. Battistig
J. Appl. Phys. Vol. 105 **(2009)**, 033501

[T3] **Formation of epitaxial SiC nanocrystals**
B. Pécz, Zs. Makkai, A. Pongrácz, I. Bársony, P. Deák and K.V. Josepovits
Surface Science, Vol. 601, Issue 13 **(2007)** p 2671

[T4] **Structural and electronic properties of Si/SiO_2 MOS structures with aligned 3C-SiC nanocrystals in the oxide**
A. Pongrácz, G. Battistig, Cs. Dücső, K.V. Josepovits and P. Deák
Materials Science and Engineering: C Vol. 27, Issues 5-8, **(2007)**, p 1444

[T5] **Nucleation of SiC nanocrystals at the Si/SiO_2 interface: Effect of the interface properties**
A. Pongrácz, G. Battistig, A. L. Tóth, Zs. Makkai, Cs. Dücső, K. V. Josepovits and I. Bársony
Journal de Physique IV, Vol. 132 **(2006)**, p.133-136

Publication in Hungarian:

[T6] **Köbös SiC nanoszemcsék epitaxiális növesztése Si-ra**
Pongracz A., V. Josepovits K., Battistig G., Makkai Zs., H. Krafcsik O., Toth A.
Kandó Konferencia **2006**, January 12-13, 2006, Budapest, Hungary
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[T7] **Formation of SiC nanocrystals at the Si/SiO_2 interface: effect of the interface properties**
A. Pongracz, A. L. Toth , G. Battistig, E. Vazsonyi, Cs. Ducso, Zs. Makkai, V. Josepovits and I. Barsony
XXXIV International School on the Physics of Semiconducting Compounds "Jaszowiec 2005" June 4-10, **2005**, Jaszowiec, Poland, Poster

[T8] **Models of regular defect structures at low index SiC/Si interfaces**
Zoltan Hajnal, Anita Pongracz, Gabor Battistig
First International Workshop on Semiconductor Nanocrystals, SEMINANO2005, September 10-12, **2005** Budapest, Hungary, Poster

[T9] **Effect of CO annealing at the Si/SiO_2 interface**
A. Pongrácz, O.H. Krafcsik, G. Battistig, Zs. Makkai, A. L. Tóth, B. Pécz, K.V. Josepovits, L. Dózsa, P. Deák
Carbon Materials Theoretical and Experimental Aspects -International Symposium **2005** Budapest, Hungary, Poster

[T10] **Control of the nucleation density of SiC nanocrystals at the Si/SiO_2 interface**
A. Pongracz, A. L. Toth , E. Vazsonyi, Zs. Makkai , G. Battistig, B. Pecz, I. Barsony and P. Deak
Fifth Int. Conf. on Advanced Semiconductor Devices and Microsystems ASDAM '04, Oct. 17-21, **2004**, Smolenice, Slovakia, Oral presentation

[T11] **Nucleation of SiC nanocrystals at the Si/SiO_2 interface: effect of the substrate orientation**
A. Pongrácz , A. L. Tóth , G. Battistig, Zs. Makkai, É. Vázsonyi, V. Josepovits and I. Eördögh
Hungarian Nanotechnology Symposium 2005 (HUNS 2005) 21-22 March, **2005**, Budapest, Hungary, Oral presentation

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[T12] **Epitaxial 3C-SiC nanocrystal formation at the SiO_2/Si interface by combined carbon implantation and annealing in CO atmosphere**
B. Pecz, J. Stoemenos, M. Voelskow, W. Skorupa, L. Dobos, A. Pongracz, G. Battistig
Journal of Applied Physics **(2009)** JR08-6178R

[T13] **Comparative investigation of the Si/SiO_2 interface layer containing SiC crystallites using spectroscopic ellipsometry, ion beam analysis and XPS**
Lohner T, Pongracz A, Khanh N Q, Krafcsik O H, Josepovits and Deak P
Physica Status Solidi (c), Vol. 5. **(2008)**. p. 1337.

[T14] **Isolated SiC nanocrystals in SiO_2**
Zs. Makkai, B. Pecz and I. Barsony and
Gy. Vida, A. Pongracz, K. V. Josepovits and P. Deak
Applied Physics Letters, Vol 86. **(2005)**, p 3109.

[T15] **Point defects in MOS structures with SiC nanocrystals**
L. Dozsa, O.H. Krafcsik, A. Pongracz, P. Deak
Silicon 2004, July 5-9. **2004.**, Irkutsk, Russia , Poster

[T16] **Electron Microscopy of SiC nanocrystals**
Zs. Makkai, Gy. Vida, K.V. Josepovits, A. Pongracz, I. Barsony, B. Pecz and P. Deak
European Microscopy Congress, Belgium, Antwerp, 21-27 August **2004.**, Poster

Further publications

[T17] **0.35 μm CMOS process on six-inch wafers - Baseline Report VI.**
L. Petho and A. Pongracz
Electrical Engineering and Computer Sciences, University of California at Berkeley Technical Report No. UCB/EECS-2008-168 December 18, **2008**

[T18] **0.35 μm CMOS process on six-inch wafers - Baseline Report V.**
A. Pongracz, G. Vida
Electrical Engineering and Computer Sciences, University of California at Berkeley Technical Report No. UCB/EECS-2007-26 February 9, **2007**

[T19] **Nanostrucure in $In_{0.2}Ga_{0.8}As$/GaAs quantum well structure**
L. Dózsa, A.L. Tóth, A. Pongrácz A.A. Koós , P. Hubik, E. Hulicius
HUngarian Nanotechnolgy Symposium 2005 (HUNS 2005) 21-22 March, **2005.**, Budapest, Hungary, Poster

[T20] **Morphological, compositional and electrical studies of β-$FeSi_2$/n-Si structures**
L. Dózsa, G. Molnár, A. L. Tóth, Z. Vértesy, Z. Osváth, Zs. J. Horváth and A. Pongrácz, P.Basa, Gy. Hárs
Engineering Aspects of Nanomaterials and Technologies, Hungarian - Korean Joint Seminar, Jan. 25-26, **2005**, BME, Budapest, Poster

[T21] **The SIMS analysis of Pd-doped porous silicon as viable material for gas sensing**
J. Saad Amar Shrair, A. Pongrácz
IV. International Workshop of Semiconductor Gas Sensors, SGS '04, Sept. 19-23. **2004.**, Ustron, Poland, Poster

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