



**FACULTY OF ELECTRICAL ENGINEERING
AND INFORMATION SCIENCE**



**INFORMATION TECHNOLOGY AND
ELECTRICAL ENGINEERING -
DEVICES AND SYSTEMS,
MATERIALS AND TECHNOLOGIES
FOR THE FUTURE**

Startseite / Index:

<http://www.db-thueringen.de/servlets/DocumentServlet?id=12391>

Impressum

- Herausgeber: Der Rektor der Technischen Universität Ilmenau
Univ.-Prof. Dr. rer. nat. habil. Peter Scharff
- Redaktion: Referat Marketing und Studentische
Angelegenheiten
Andrea Schneider
- Fakultät für Elektrotechnik und Informationstechnik
Susanne Jakob
Dipl.-Ing. Helge Drumm
- Redaktionsschluss: 07. Juli 2006
- Technische Realisierung (CD-Rom-Ausgabe):
Institut für Medientechnik an der TU Ilmenau
Dipl.-Ing. Christian Weigel
Dipl.-Ing. Marco Albrecht
Dipl.-Ing. Helge Drumm
- Technische Realisierung (Online-Ausgabe):
Universitätsbibliothek Ilmenau
[ilmedia](#)
Postfach 10 05 65
98684 Ilmenau
- Verlag:  Verlag ISLE, Betriebsstätte des ISLE e.V.
Werner-von-Siemens-Str. 16
98693 Ilmenau

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ISBN (Druckausgabe): 3-938843-15-2
ISBN (CD-Rom-Ausgabe): 3-938843-16-0

Startseite / Index:

<http://www.db-thueringen.de/servlets/DocumentServlet?id=12391>

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Self organization and properties of Black Silicon

1 Introduction

If the geometrical confinement of solid state materials reaches the characteristic length scale determining the macroscopic mechanical, chemical, optical and electronic properties, a drastic change in the behavior of the material occurs. The most known effect is the quantization of density of states in semiconductor materials. This effect is used in a wide range of electronic and optoelectronic devices. They are fabricated by using the classical top down approach developed over years in the semiconductor industry. An alternative possibility to form confined and nanostructured systems is the bottom up approach. This method uses the principles of self organization at microscopic scale to form structured systems in homogeneous environments. A typical example for this method is the self organization of quantum dots used as active layers in solid state lasers. Here, a bottom up approach will be reported leading to self formation of dense arrays of silicon needles with scalable properties– the so called Black Silicon. This modified silicon based material has a wide range of application in the field of optical absorber elements [1], anti-reflective coatings, field emitter arrays [2], superhydrophobic surfaces, in catalytic enhanced microreactors and for new bonding technologies based on the Velcro[®] effect [3].

2 Technologies

The Black Silicon was fabricated by using two different types of dry plasma based etching processes.

The first method is a modified reactive ion etching (RIE) process known from the fabrication of vertical side wall geometries by tuning the sensitive relationship between etching and passivation during structuring toward the passivation. For the preparation of the silicon needles the surface of a polished 100 mm silicon substrate was structured in a parallel plate reactor (STS 310/320 twin system) from Surface Technology Systems Ltd., UK. The assembly of the etching chamber consists of a top electrode, with a modified gas inlet for high needle uniformity and a cooled substrate electrode powered by an auto matched RF power supply. For controlling the ion energy a self-bias voltage generated

by a 100 W RF power supply at 13.56 MHz capacitively coupled to substrate electrode was selected. The self bias at these conditions was 120V. Sulfur hexafluoride and oxygen were used as etching gases. The etching process is based on both etching components, the attack by reactive gas radicals (chemical part) and bombardment with positive, high-energy ions (physical part). Both, the natural silicon oxide on the substrate and the passivation layer (SiO_xF_y) deposited simultaneously, due to local plasma inhomogeneities and nucleation conditions form an inhomogeneous layer system on the plasma treated surface. This led to an incomplete removal of the passivation system. The left-over of the oxide and the passivation layer act as micromasks leading to Si needle formation.

The needle formation was analyzed by varying the plasma parameters within the ranges shown in table 1.

Table 1: Process parameters for needle formation with RIE

	etching parameter
SF ₆ gas flow [sccm]	65 ... 75
O ₂ gas flow [sccm]	20 ... 25
platen power [W]	100
chamber pressure [mTorr]	50
chamber temperature [°C]	50
substrate temperature [°C]	20 ... 30
process time [min]	1 ... 5

Constant needle densities of up to 4 Million needles per mm² were obtained for full 4" substrates surfaces (Fig. 2, left). The length of the resulting tips is a function of the etching time. A saturation effect is induced by longer diffusion paths of the etchants into the gaps of the needles. Needle lengths up to 5µm are possible.

The second process investigated for needle fabrication is a modified advanced silicon etching process (ASE[®]) in an inductively coupled plasma (ICP) multiplex system from Surface Technology Systems Ltd. too.

The ICP system consists of a process chamber with a mechanical wafer clamping system and a loadlock chamber. The substrate electrode and the wafer backside are cooled to room temperature. The heat transfer is supported by helium between the wafer and the chuck. The inductive coil which is connected to a 13.56 MHz RF power supply generates a high-density plasma. For controlling the ion energy, a bias voltage induced by RF power at 13.56 MHz is capacitively coupled to the platen electrode and therefore to the wafer.

The needle formation was studied by varying the process parameters including cycle

times, coil and platen power, substrate temperature and process time as shown in table 2.

Table 2: Process parameters for needle formation with ASE ICP

	passivation	etching
C ₄ F ₈ gas flow [sccm]	85	-
SF ₆ gas flow [sccm]	-	130
O ₂ gas flow [sccm]	-	13
cycle time [s]	10 ... 16	9
coil power [W]	500 ... 600	500 ... 600
platen power [W]	-	10 ... 20
chamber pressure [mTorr]	18	38
chamber temperature [°C]	40	
substrate temperature [°C]	20 ... 30	
Process time [min]	15 ... 40	

As a result of this etching process, silicon needles with a length up to several micrometers are formed. They have a homogenous distribution over large areas up to full 4" wafers (see fig. 2, right). The density is in the range of 2-3 Million needles per mm² with needle diameters between 500-700 nm.

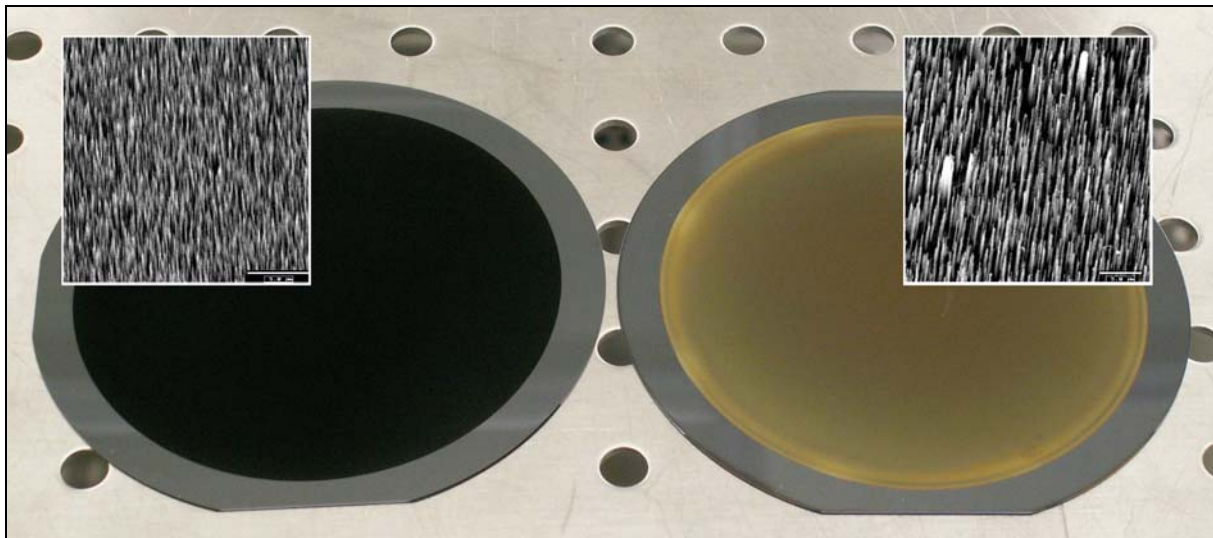


Fig. 2: Constant needle densities on 4" substrates with RIE (left) and ASE ICP (right)

3 Black Silicon Formation Model

In both Black Silicon technologies the self-formation of the silicon needles occurs as a consequence of spatial inhomogeneities in deposition and etching processes during plasma processing caused by the specific interactions of nucleation and deposition of the passivation system and the removal by ion bombardment and chemical etching [4-13]. As a consequence of the interaction of the different spatial inhomogeneities a high density of etching residues or the passivation layer formed during the early stages of the etching process. The local passivation acts as self masked areas causing the Black Silicon formation. In the case of RIE processing all processes act simultaneously, whereas in the case of ICP processing the needles are formed by alternating between passivation of the horizontal surface and etching of the unpassivated silicon. A simplified scheme of this formation process is shown in Fig. 3.

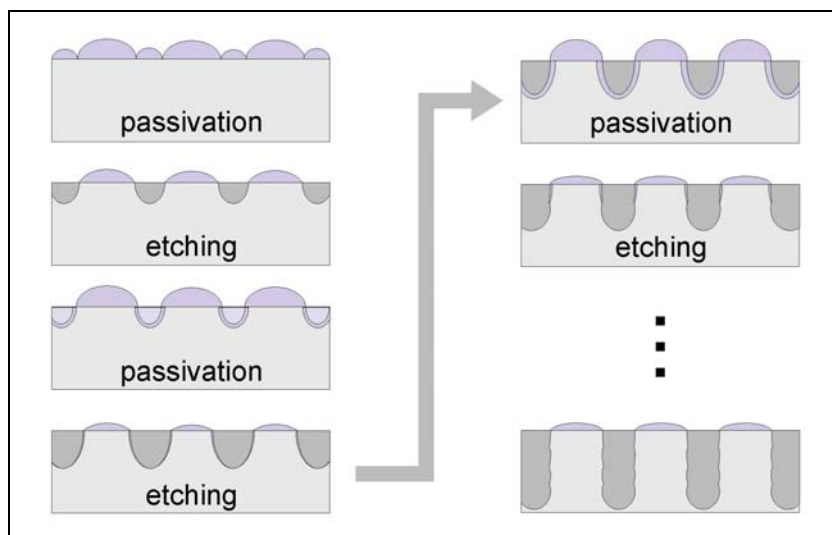


Fig. 3: Process cycle for needle formation with ASE® ICP

4 Characterization

The resulting structures were investigated by transmission electron microscopy (TEM, Tecnai®), scanning electron microscopy (SEM), Auger electron spectroscopy (AES) and ellipsometry by using a SE 801 from Sentech to access the structural, morphological, compositional properties and optical properties of the nanostructured needles.

The needles of the Black Silicon formed by the RIE process exhibit a regular cone like shape with smooth needle surfaces (Fig. 4). The average radius of the tip was determined from the TEM and IFFT around 5 nm. All needles are well aligned and exhibit the same orientation as the silicon substrate.

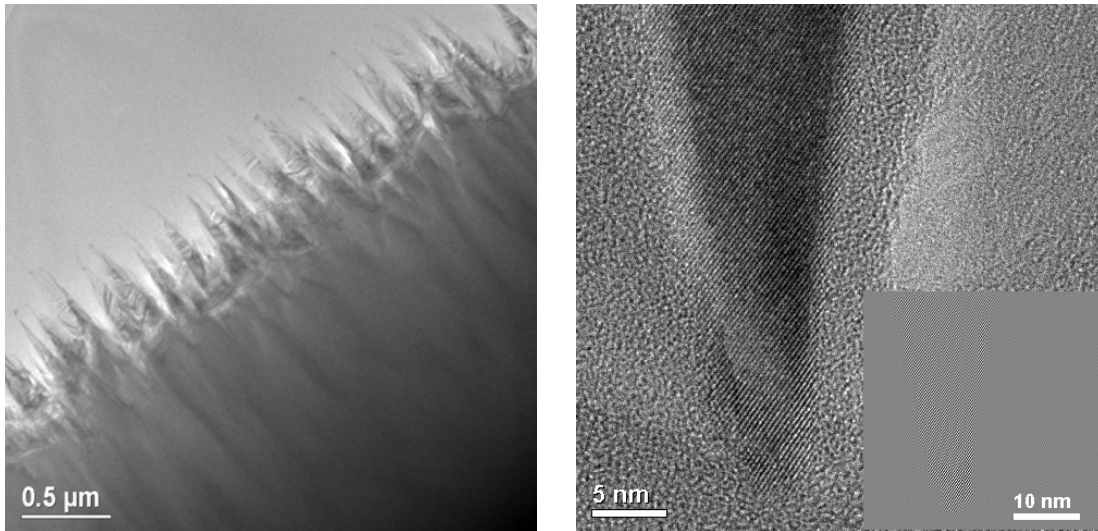


Fig. 4: Overall (left), high resolution (right) TEM micrograph and an inverse Fourier transformed image (IFFT) as an inset in the right pattern of Black Silicon formed by the RIE method.

The crystal structure of the formed needles exhibit no dislocation and two dimensional defects, i.e. the RIE process preserves the single crystalline structure and only the formation of point defects in the region corresponding to the penetration depth of the ions can be expected.

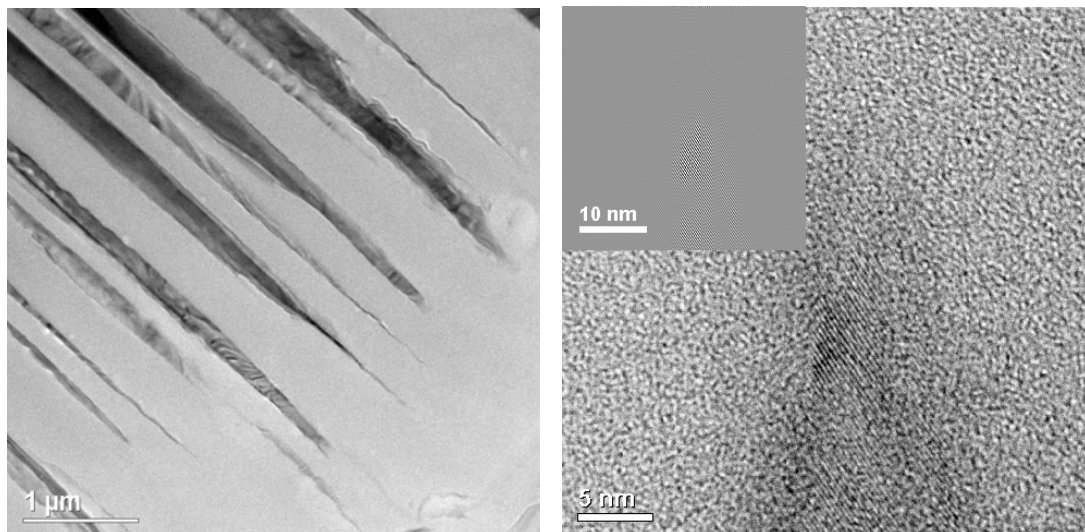


Fig. 5: Overall (left), high resolution (right) TEM micrograph and IFFT pattern as an inset in the right pattern of Black Silicon formed by the ASE® ICP method.

The needles formed by the ASE® ICP show a larger needle diameter, a broader distribution in the needle dimensions and a stronger needle height variation compared to the RIE process (Figs. 4 and 5). The surface of the formed needles show an irregular behavior in form of a saw tooth profile. Nevertheless, as in the case of RIE processing the needles do not contain visible crystallographic defects. The alignment of the needles

exhibit a strong twist and tilt caused by larger Black Silicon thickness compared to the thickness of the Black Silicon formed by the RIE method. Nevertheless, the tip curvature was as small as in the case of the RIE process, namely around 5 nm.

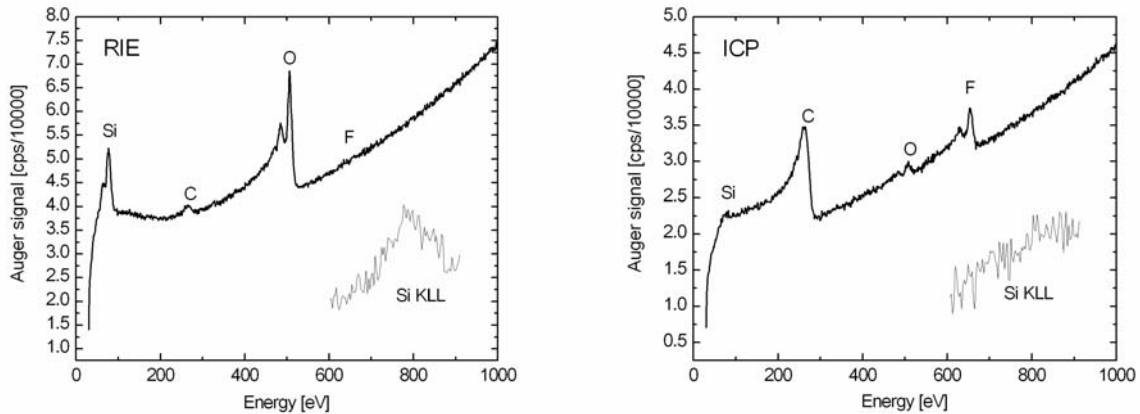


Fig. 6: Integral large area Auger electron spectroscopy measurements of the RIE (left) and ASE[®] ICP (right) formed Black Silicon.

The origin of the passivation depends on the chosen preparation process and the plasma chemistry. In the case of the RIE process only strong oxygen and silicon peaks were found with small carbon peak (Fig. 6, left). Flour was found to be close to the detection limit. This indicates a silicon dioxide passivation during the formation process. The observed carbon peak can be mainly related to carbon contaminations due to the transportation through air into the AES equipment. For the ASE[®] ICP prepared Black Silicon a quite different AES spectra was obtained (Fig. 6, right). The spectra shows strong carbon and flour peaks and nearly no silicon and a weak oxygen peak. The observed AES peaks indicate a carbon fluoride (Teflon) coverage of the needle tips as well as the needle side walls. Furthermore, the silicon KLL peak was observed to be not detectable in comparison to the Si KLL peak in the case of the RIE sample. The Auger electrons contributing to the Si KLL peak (3.5 nm) have a larger inelastic mean free path than the Auger electrons of the Si LVV peak (0.5 nm). This means that the carbon fluoride layer thickness is below 10 nm. This carbon fluoride layer passivates the surface and inhibits the interaction of the surface with oxygen. Additional AES depth profiling studies have to be carried out to verify if this layer on the ASE[®] ICP needles is homogeneous or if there is any carbon fluoride – silicon dioxide layer on top of the needles. In Fig. 7 the imaginary part of the pseudodielectric function is shown. For comparison the imaginary part of the dielectric function of crystalline and amorphous silicon is also displayed. The ellipsometric data were obtained in an energy range from 1.5 to 4.4 eV with a spectroscopic ellipsometer with a rotating analyzer. The information depth in this

energy range varies strongly with photon energy ranging from 5 nm at 4.2 eV to several 100 nm. The obtained data were converted into the pseudodielectric function [15]. The pseudodielectric function describes the effective response of the layer and the substrate to the incident light. From Fig. 7 it is evident that bulk contributions to the spectra can be neglected due to the absence of thickness oscillations.

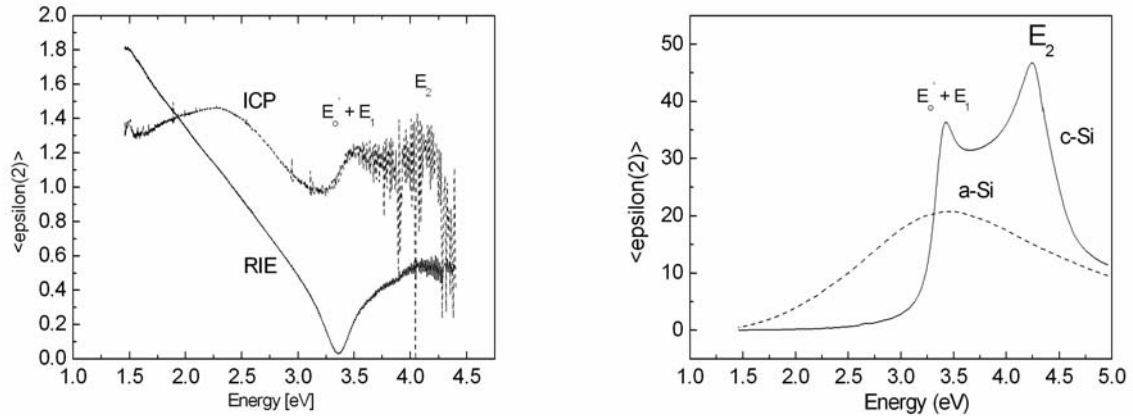


Fig. 7: Imaginary part of the pseudodielectric function of the Black Silicon formed by RIE and ASE[®] ICP (left) and imaginary part of the dielectric function of crystalline (c-Si) and amorphous silicon (a-Si) (right).

The obtained lineshapes are qualitatively different from the lineshapes of crystalline and amorphous silicon. For both types of preparations a strong reduction of the amplitude in the imaginary part of the dielectric function can be found. In the case of the ICP the high energy region near the critical points resembles the form of the crystalline silicon spectra and spectral features which can be related to the $E_0 + E_1$ and E_2 critical can be observed. A line shape analysis of the spectra in this region revealed a shift of the critical points from 3.4 to 3.5 eV in the case of $E_0 + E_1$. A similar shift of 0.1 eV to higher energies was found in the case of E_2 . For the RIE Black Silicon the $E_0 + E_1$ feature in the spectra is recognizable only as a shoulder on the broad peak around 4.2 eV. Such behavior was reported for porous silicon [16]. The E_2 peak shifts to higher energy compared to crystalline silicon.

In the pseudodielectric function beside the surface roughness and the chemical composition of the surface two different contributions may affect the lineshape of the spectra, namely a bulk like contribution of the silicon needles and a carrier confinement effect in the needle tip. The bulk like contribution is stronger in the case of the ICP prepared samples due to the lower density of the needles and the larger needle diameter. The confinement effects in the needle tips superpose on bulk contribution of the structure led to a slight shift of the critical points in the spectra. In contrary, the RIE needles show a

stronger contribution of the nanocrystalline carrier confinement leading to a shift of the E_2 gap to higher energies and to a vanishing of the $E'_0 + E_1$ structure due to the higher density of the formed silicon structures. The observed behavior is similar to micro-porous silicon [17, 18].

4 Conclusions

Different types of Black Silicon were formed by using two different dry etching methods. The density and the surface composition of the needles depend strongly on the formation conditions. The tips of the different needles show no detectable difference in their curvature. Ellipsometric measurements revealed that the pseudodielectric function of the Black Silicon is largely affected by confinement effects and behaves similar to micro-porous silicon.

Acknowledgement: The authors acknowledge the patient TEM sample preparation by Mrs. Elvira Remdt.

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