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The role of the interfaces in the optical effects of large-sized $SiC_xO_{1-x}N$ nanocrystallites

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ABSTRACT

The band energy structure of large-sized (10-25) nm nanocrystallites (NC) of $SiC_xO_{1-x}N$ (0.96<x<1.06) was investigated using different band energy approaches, as well as modified Car Parinello molecular dynamics simulations of interfaces. A thin carbon sheet (of about 1 nm) appears, covering the crystallites. This sheet leads to substantial reconstruction of the near-the-interface $SiC_xO_{1-x}N$ crystalline layers. Numerical modeling shows that these NC may be treated as quantum dot-like $SiC_xO_{1-x}N$ reconstructed crystalline surfaces, covering the appropriate crystallites. All band energy calculation approaches (semi-empirical pseudopotential, fully augmented plane waves and norm-conserving self-consistent pseudopotential approaches) predicted the experimental spectroscopic data. In particular, it was shown that the near-the-surface carbon sheet plays a dominant role in the behavior of the reconstructed band energy structure. Independent evidence for the important role of the dot-like crystalline layers are the excitonic-like states, which are not dependent on the particular structure of the SiC, but are sensitive to the thickness of the carbon layer.

INTRODUCTION

There has recently been increased interest in the possibility of using nano-technologies as materials for optics and electronics, the main reason being the size-dependent electronic and optical properties of these materials [1-4]. The properties of large-size nanocrystallites (larger than 10 nm) were treated as the so-called superposition of the NC and other structures [5-8]. One can predict that the latter will be directly dependent on the relative sizes of particular crystallites and the surrounding interface environment. Depending on these parameters, we will obtain different excitonic states which define the behavior of the interface band energy gradients. The coexistence of bulk-like and quantum confinement states presents the possibility of working with electron energy dispersion within the same crystallites contrary to the thin $SiC_xO_{1-x}N$ films deposited on the $SiC_xO_{1-x}N$ crystalline surfaces.

Among the many possible NC materials, $SiC_xO_{1-x}N$ crystallites were chosen because the technology for their manufacture with the sizes needed is well developed, the energy gap of $SiC_xO_{1-x}N$ may be manipulated within the large spectral ranges (2 – 4.5 eV), depending on polytype kinds, and because $SiC_xO_{1-x}N$ is substantially more stable than other SiON materials, when external mechanical and thermo-treatments are applied.

The main goal of the present work was to study the optical properties of $SiC_xO_{1-x}N$ NC, both experimentally, as well as theoretically. In particular, we investigated the influence of nanocrystallite size and carbon excess on the optical absorption of the $SiC_xO_{1-x}N$ nanocrystallites, the contribution of the reconstructed near-interface states to the visible absorption of the NC and the contribution of the carbon sheet interfaces to the absorption spectra observed.

The nanopowders were synthesized by CO_2 laser pyrolysis of silane and acetylene gaseous mixtures. The reactant fluxes monitored the ratio C/O and induced a carbon or silicon-rich network in the outer-most SiC nanoparticle surfaces.

Size-dependent effects are usually studied for NC with sizes below 8 - 10 nm, where clear size-confined effects are observed. In such cases, **k**- space bulk-like dispersion disappears and

discrete excitonic-like levels in the energy gaps appear. However, interface (reconstructed) dot-like states corresponding to an intermediate level, with both bulk-like, as well as dot-like quantised excitonic, properties can be promising in detecting experimentally obtained optical phenomena. These interface sheets are formed by reconstructed $SiC_xO_{1-x}N$ crystalline films separating the bulk-like and thin carbon layers.

On the basis of the relative presence of quantum dot states, one can estimate the relative contributions of reconstructed $SiC_xO_{1-x}N$ near-the–interface structural fragments to the band energy (BE) dispersion, as well as that of the excitonic state to the optical absorption [9-12] (being directly connected to the imaginary part of the dielectric susceptibilities).

RESULTS AND DISCUSSION

The SiCON nanocrystallite specimens were monitored using TEM, NMR, Raman and IR methods. Optical absorption caused both by band energy reconstruction, as well as by excitonic effects, is analyzed. The role of carbon excess was demonstrated experimentally by increasing the C/O ration over the C-rich particle surfaces.
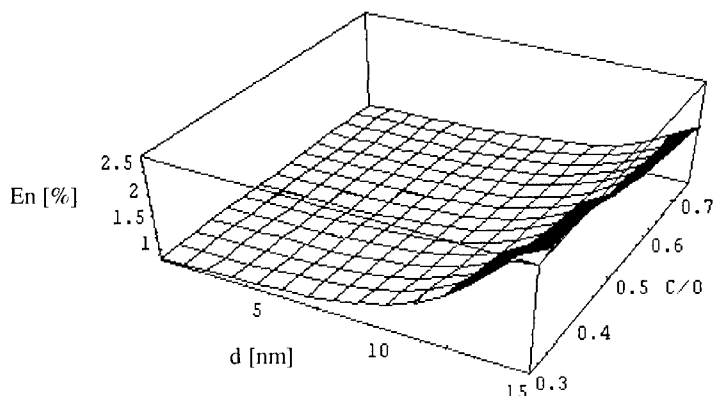

Figure 1. The relative contribution of the interfaces to the energy gap is presented dependent on the crystallite sizes d and ratio of the C/O.

In Fig. 2 the band energy dispersion for the interfaces in the case of the x=1.02 are presented. One can see substantial reconstruction of the band energy dispersion near the interfaces. Moreover the energy dispersion derivative is varied. This fact is caused by the reconstruction of the near-the surface states [13-16].
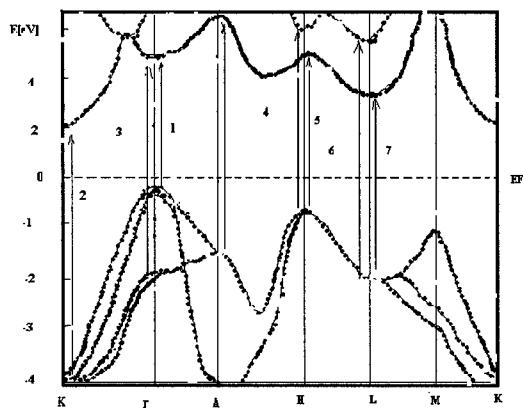
Figure 2. Band structure of the SiC$_x$O$_{1-x}$N for the x=1.02. The points indicate the bands corresponding to the reconstructed surfaces.
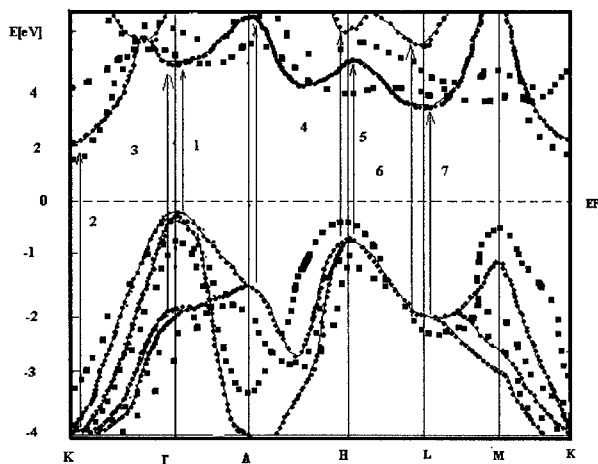

Figure 3. Band structure of the SiC$_x$O$_{1-x}$N assuming an interface thickness of about 0.6 nm.

Fig. 3 shows additional band structure reconstruction when we undergo to the bands more close to the interfaces. This correlates well with the charge density distributions near the interfaces (see Fig. 4). One can see that a shift toward the deep interface levels stimulates additional charge density re-distribution.
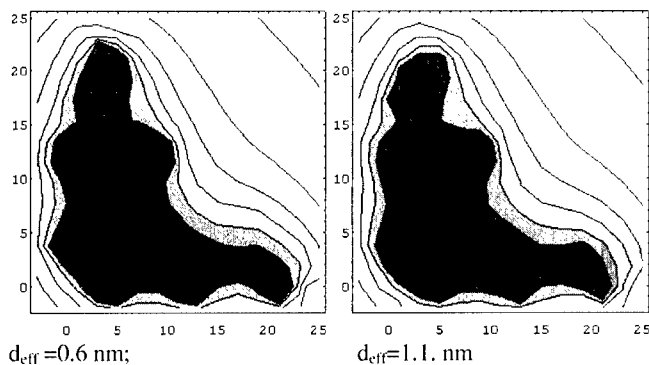
$d_{eff} = 0.6$ nm; $d_{eff} = 1.1.$ nm

Figure 4. Reconstruction of the near-the-interface charge density distribution.

This fact confirms the layered dot-like structure of the investigated nanocrystallites. Our investigations have shown that the dominant role in the optical spectra observed is played by the dot-like near-the–surface states which form strong sharp-like absorption excitonic
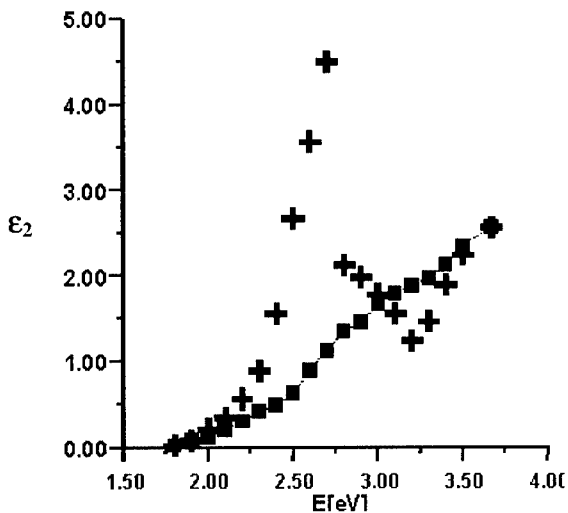

Figure 5 . Excitonic spectra at LHeT - + and RT - ■.

spectra (Fig. 5). From Fig. 5 one can see an occurrence of the dot-like excitons playing a key role in the observed spectra.

The connected with the measured behaviours the dependencies of the transparency T versus the film thickness and O/C ratio at LHeT are presented in the Fig. 6.
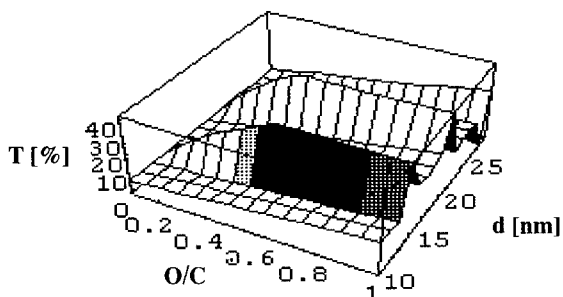
Figure 6. Typical dependencies of the transparency versus the O/C ratio and film thickness.

One can see that T possess modulated-like dependence versus the thickness d. This reflects an increase of competition between the long-range ordering and short-range disordering.

CONCLUSIONS

1. Our investigations have shown that the materials investigated have interface thin layers with thickness of about 1.5 nm. This layer may be considered as a reconstructed surface of the Si by the covered films.
2. The obtained results present new opportunities in semiconductor electronics, making it possible, for example, to receive 3D memory for computers on the trapping levels.
3. The calculations we made using the *ab initio* Car-Parinello method are an additional confirmation of the new type of the interfaces that will shortly find application in the electronic technique.
4. The simulations carried out predict the modulated-like features of the transparency versus the film thickness and O/C ratio.

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