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FORMATION OF LIGHT-EMITTING STRUCTURES BASED ON SILICON NITRIDE LAYERS ON SILICON

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The physical fundamentals of the development of new materials and technologies are currently in the center of attention for many researchers. By controlling the size of the structural components of a material, it becomes possible to produce qualitatively new electronic devices.

The radiative properties of silicon nanoparticles in the visible range are of the considerable interest.

Silicon nitride is one of the main dielectrics in integrated circuits with a band gap of ~ 5.3 eV. This material is more suitable for the development of electroluminescent devices compared to SiO_2 ($E_g = 8.2$ eV).

Initially, the interest to the light-emitting properties of silicon nitride arose during the formation of the system “Si nanoclusters in a dielectric matrix” on its basis. Indeed, such a system exhibits intensive luminescence. However, the silicon nitride matrix luminesces itself, and the nature of this radiation is being widely discussed in the literature.

In connection with the foregoing, in this work, it seems appropriate to expand research in the field of creating a light-emitting structure based on silicon nitride enriched with silicon.

The structure of crystalline and amorphous Si_3N_4

Silicon nitride is a refractory compound with a predominantly covalent type of bonds. Si_3N_4 is a polymorphic compound that exists in three modifications. In the crystalline state, there are two hexagonal phases: α - and β - Si_3N_4 (figure 1), with the structure of phenacite [1].

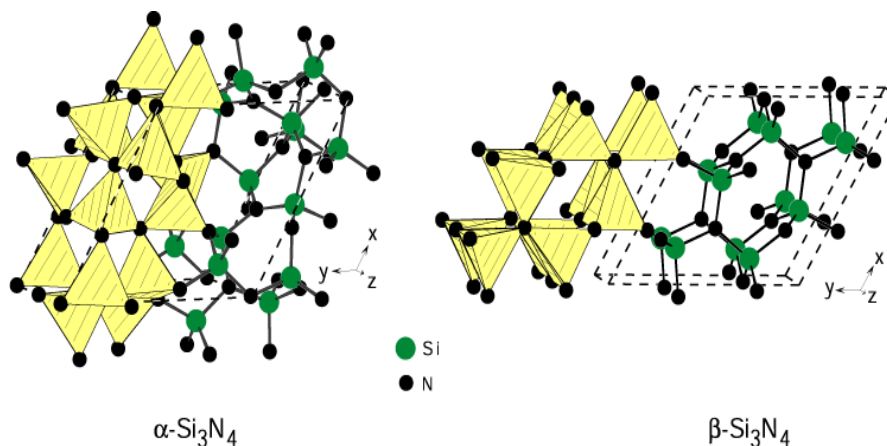


Figure 1 - α - Si_3N_4 and β - Si_3N_4 unit cells

At temperatures below 1150°C , the β -phase is stable; at higher temperatures, the α -phase is stable. The density of these phases is almost the same $3.1\text{-}3.2\text{ g}\cdot\text{cm}^{-3}$.

The cubic γ -modification was obtained at a pressure of 15 GPa and a temperature above 1700°C by the method of laser heating in a diamond cell. In the literature, this modification is referred to as the c-modification. It has a spinel-type structure in which two silicon atoms have an octahedral coordination with six nitrogen atoms, one silicon atom is coordinated tetrahedrally with four nitrogen atoms (figure 2). It is theoretically shown that this structure should have a high hardness, similar to that of a diamond and c-BN [2].

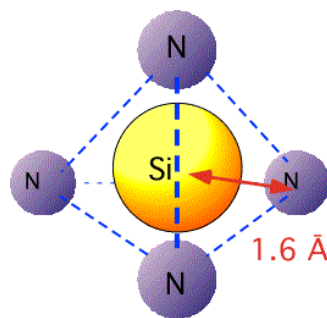


Figure 2 - The main structural unit of Si_3N_4

In the work [ref.] Gritsenko V.A. reports the parameters of elementary cells of α - and β - modifications. The unit cell of α - Si_3N_4 contains 28 atoms (12 Si and 16N) and has lattice constants $a = 7.75\text{ \AA}$ and $c = 5.62\text{ \AA}$. The β - Si_3N_4 cell contains 14 atoms (6 Si and 8 N), the lattice constants, $a = 7.71\text{ \AA}$, $c = 2.91\text{ \AA}$. By the symmetry, α - Si_3N_4 is referred to $P31c$ space group, β - Si_3N_4 - $P63/m$. Both phases have a tetrahedral structure.

Non-stoichiometric silicon nitride (SiN_x) differs from stoichiometric nitride (Si_3N_4) by the amount of excess silicon in the composition (Si_{exc}) [3].

$$\text{Si}_{\text{exc.}} = \frac{\text{Si}_{\text{at.}\%}}{\text{Si}_{\text{at.}\%} + \text{N}_{\text{at.}\%}} - \frac{3}{7}$$

Luminescence of defects. Edge luminescence

In recent years, a number of studies have appeared in which PL of silicon nitride is associated with radiative transitions between the energy levels of defects [4].

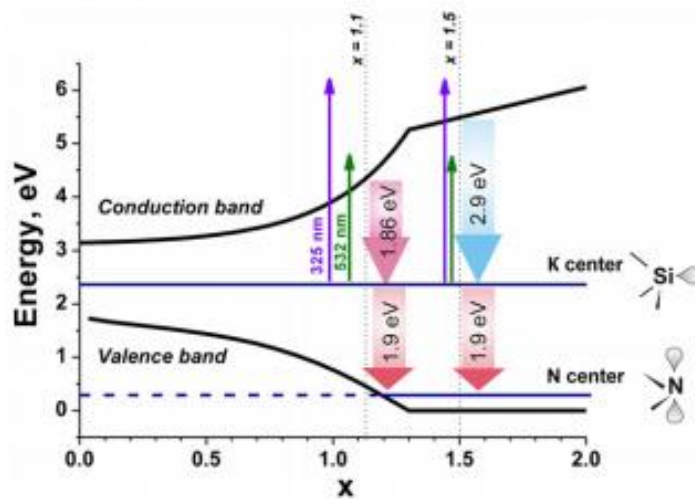


Figure 3 - Model of possible optical transitions based on the Robertson's band diagram for amorphous SiN_x

In this case, the K- and N- centers act as the main centers of radiative recombination. The K-center is an intrinsic defect in the silicon nitride matrix, which is a silicon atom bound to three nitrogen atoms ($\text{N}_3=\text{Si} \bullet$). The presence of K-centers in the silicon nitride matrix can lead to luminescence in the range of 2.5 ± 0.1 eV (478–517 nm). The N-center is a two-coordinated nitrogen atom ($\text{Si}_2 = \text{N} \bullet$).

These centers are already present in the initial silicon nitride films, but their number increases noticeably after high-temperature annealing as a result of the dissociation of the N-H bonds [5].

The energy of electronic transitions with the participation of K-centers is 2.1–2.6 eV; therefore, the luminescence in the green region (470–590 nm) is often attributed to the K-centers [6].

In the model of edge luminescence, there is a process of transition of excited carriers to neighboring localized states with lower energy, followed by the light emission. In amorphous materials, there is only a short-range order. Therefore, in these materials, one can observe new phenomena, which are explained by the presence of localized electronic states. The energy levels of these localized states lie near the bands edges, expanding them into the region of the bandgap. The formation of localized states in amorphous silicon nitride, in contrast to crystalline states, leads to a higher photosensitivity and the appearance of PL due to radiative recombination of charges localized at the band edges.

This model was quite successfully applied to explain PL and its shift with increasing concentration of Si in SRN films, in which Si nanoclusters were not detected by high-resolution transmission electron microscopy (TEM). Using this model, researchers managed to explain the position of the PL band and the change in the PL intensity depending on the composition of the nitride film [7].

The intensity and the spectral range of PL in silicon nitride films strongly depend on the regimes and conditions of deposition, as well as on subsequent heat treatments.

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