

When laser fabrication technology meets semimetal and semiconducting silicides: advanced transparent conductors and optical absorbers

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Despite advanced optical materials conquering the modern landscape of photonics and optoelectronics, silicon (Si) remains tightly as a main building block dominating in both science and market. However, the rigid semiconducting properties of the monocrystalline Si place its optoelectronics efficiency even far beyond theoretically predicted value in accordance with Shockley-Queiser limit, if one considers the solar cell application field. Another example is associated with Si predominantly isotropic properties in all the diversity of optical phenomena due to the centrosymmetric crystal lattice of cubic diamond type. Finally, there is a long-standing demand to combine Si CMOS technology and photonics to introduce a high-level integration into optical circuits. However, the difficulties in constructing effective and pure Si-based light emitters and sensors operated in the near infrared spectral range still have a sizable effect. The reasons are in the indirect nature and the value of Si band gap.

Fortunately, the solution lies on the surface being in a class of materials called silicides. It has long been known that semiconducting silicides possess great potential in the field of photovoltaics and optoelectronics [1], while their metallic counterparts are used for low resistive interconnects [2]. Owing to a simplicity of the silicidation process and additional “green” motivation, silicides has enriched scientific community with a so-called silicon-silicide approach in developing the next generation solar cells [3,4], photodetectors [5,6], light-emitting diodes [7,8] and other active and passive components [9,10].

The next great challenge has rose when the modern Si technology, especially solar cells, has been narrowed down to the motto “thinner & cheaper”, resulted in a need to minimize optical losses associated with reduced absorbance of extremely thin Si layers and to balance perfectly the optical transparency and electrical conductivity of the any electrode materials applied in the diversity of Si-based devices.

In this regard, laser technologies could give a push towards further advancing of the mentioned above silicon-silicide approach. For example, a high performance transparent electrode of mesh type has been fabricated from the thin semimetal film of calcium disilicide (CaSi_2) by flat-top beam shaped selective laser ablation with high precision [11]. Of importance, that this perforated electrode not only demonstrated an increased optical transparency ranging from visible to middle infrared spectral ranges, while maintaining high electrical conductivity, but was naturally integrated with Si photovoltaics and optoelectronics, which resulted in Si photodetector with enhanced photoresponse and extended operated spectral range [12]. Next example is related with silicidation of the laser-induced periodic surface structures (LIPSSs) and spikes imprinted on Si surface [13] to drastically enhance its optical absorption and thus photoresponse below the Si band gap, which is 1.12 eV. Actually, when dealing with silicidation of Si within magnesium (Mg), one could obtain a magnesium half-silicide (Mg_2Si) with narrow band gap of 0.7 eV covering LIPSSs or spikes preserving both

periodicity and antireflection morphology [14]. As a result, this bottom-up approach (covering LIPSSs rather than direct laser processing of the final material – silicide) resulted in Si-based photodetector with a record (for the silicides) photoresponse in the wide spectral range and modality of polarization sensitive photoresponse in the near-infrared range, when Mg-silicidation took place atop Si spikes and LIPSSs, respectively. Finally, replacing Mg with Ca, it is possible to get CaSi_2 /spiky Si nanostructures with low emissivity in the infrared, while maintaining a low reflectivity in the visible spectral ranges. It opens the door for the design of Si-based nanostructured materials with high photothermal and hybrid photothermoelectric conversion efficiencies.

In summary, there is still plenty of room to endow Si with different modalities such as infrared sensitivity, naturally integrated transparent conducting electrodes with high figure of merit and solution to circumvent some basic symmetry related restrictions. This report proposes to combine laser processing and Si-silicide approach towards a future key technology. As a proofs-of-the-concept, Si-silicides photodetectors with polarization sensitivity, extended spectral range, reduced optical losses and enhanced detectivity in addition to optical absorbers with high photothermal conversion efficiency were demonstrated.

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