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Wide-Band “Black Silicon” with Atomic Layer Deposited NbN

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Abstract — **Antireflection surfaces are often utilized in optical components to reduce undesired reflection and increase absorption. We report on black silicon (b-Si) with dramatically enhanced absorption over a broad wavelength range (250–2500 nm) achieved by applying a 10–15 nm conformal coating of NbN with atomic layer deposition (ALD). The improvement is especially pronounced in the near infrared (NIR) range of 1100–2500 nm where absorption is increased by >90%. A significant increase of absorption is also observed over the ultraviolet (UV) range of 200–400 nm. Preceding NbN deposition with a nanostructured ALD Al_2O_3 (n-Al_2O_3) coating to enhance the NbN texture was also examined. Such texturing further improves absorption in the NIR, especially at longer wavelengths, strong absorption up to 4–5 µm wavelengths has been attested. For comparison, double side polished silicon and sapphire coated with 10 nm-thick NbN exhibited absorption of only ~55% in the NIR range of 1100–2500 nm. The results suggest a positive correlation between the surface area of NbN coating and optical absorption. Based on the wide-band absorption, the presented NbN-coated b-Si may be an attractive candidate for use in e.g. spectroscopic systems, infrared microbolometers.**

Index Terms* — *black silicon, wide-band absorption, infrared absorption, atomic layer deposition, NbN, grass-like alumina

I. Introduction

Silicon is widely used for photodetector and photovoltaic applications [1], [2]. High reflectance losses up to 40% however severely impede the performance of silicon optical devices [3]. Surface texturing of silicon by reactive ion etching has been introduced in order to reduce optical reflection and enhance optical absorption [3], [4]. This technique produces black silicon (b-Si) with good antireflection properties in the range 400–1000 nm. However, the silicon bandgap of 1.11 eV [5] limits the absorption of wavelengths above 1100 nm and render the texturing techniques as largely ineffective for these wavelengths. To address this, microstructuring and hyperdoping of silicon with femtosecond laser pulses in SF_6 or Cl_2 has been developed [6]–[8]. Although good absorption properties in the infrared were demonstrated, the high cost and complexity of this technique inhibits widespread adoption. More recently, less complex and cheaper techniques for increasing infrared absorption have been introduced based on chemical etching [9]–[13].

Another approach for enhancing infrared absorption of silicon was recently presented and consisted of coating b-Si structure with pyrolytic carbon [14]. Reflectance below 0.5% was shown in the 350–2000 nm wavelength range.

Niobium nitride (NbN) is known to absorb light in visible and near infrared (NIR) [15], [16] regions, it is a metallic material with relatively high n and k values [15] and superconducting properties [16], [17]. NbN is a common material for single photon detectors operating in NIR region [18]–[21] and it is also used in absorbing antireflective coatings [22]. This makes NbN an attractive candidate for NIR absorption enhancement.

In this work, we present a technique to dramatically increase the absorption of b-Si in the near infrared region by applying a thin coating of NbN using atomic layer deposition (ALD). We show that the high absorption is due to the synergetic combination of both the microstructure of b-Si and NbN, and not from the NbN alone, by comparing the coated b-Si with NbN coated double side polished (DSP) silicon and DSP sapphire. We further enhance the absorption in the near infrared by introducing a layer of grass-like alumina [23] on b-Si in order to increase the surface area of NbN film.

II. Experimental

B-Si was fabricated by etching the silicon surface with a gas mixture of SF_6/O_2 at −110 °C using an inductively coupled plasma reactive-ion etcher (ICP-RIE Plasmalab 100 by Oxford Instruments) [24]. DSP silicon wafers were used for b-Si fabrication, and only one side of the wafers was etched. Etching was performed at 10 mTorr pressure with SF_6/O_2 flows of 40/18 sccm respectively, plasma ignition power of 1000 W and a forward power of 6 W. This etching produces sharp conical microstructures from the silicon surface [4].

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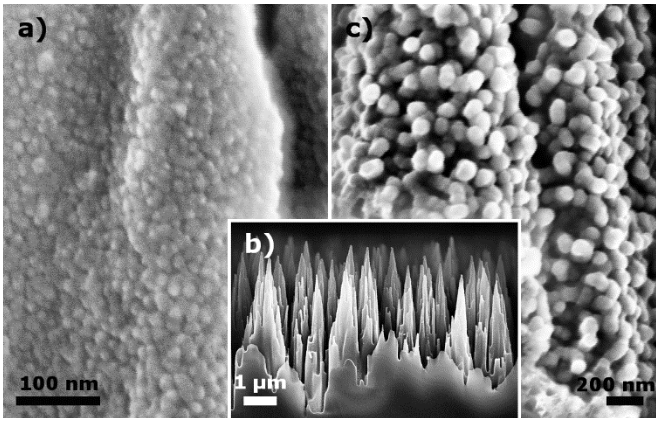

Fig. 1 SEM images of: a) b-Si surface after coating with 10 nm ALD NbN; b) b-Si coated with NbN; c) nanostructured NbN coating on b-Si.

After creation of the b-Si, the wafers were coated with either 10 or 15 nm of NbN by ALD (Sunale R-200 by Picosun). The deposition was performed at 450 °C using $NbCl_5$ and NH_3 as reactants at a pressure of ~2 mbar. Scanning electron microscope (SEM) image of the b-Si surface after being coated with 10 nm of NbN is presented in Figure 1a. Figure 1b shows the same sample in a large scale to display the structure of b-Si. It is observed that the deposited NbN film initiates as island growth, which is attributed to the fact that not enough ALD cycles have been executed to produce a continuous film. [25], [26] Thicker NbN coatings are smooth continuous films with lower surface area NbN coatings are smooth continuous films with lower surface area and lacking in small scale topographical features. Contrarily, thinner NbN coatings provide less NIR absorptive material.

Another set of samples was manufactured with grass-like alumina [23] intermediate layer, in which 5 or 10 nm of Al_2O_3 were deposited by ALD (TFS 500 by Beneq) on top of b-Si. These samples were immersed into de-ionized water at 65 °C for 30 min to transform Al_2O_3 into nanoporous, grass-like state as described elsewhere [23]. After that 15 nm of NbN was deposited in the same way as described above. The surface of b-Si coated with nanostructured NbN is presented in Figure 1c. The grass-like Al_2O_3 serves as a dramatic enhancement in the surface area of the substrate prior to NbN deposition. Notably, NbN did not experience island growth on Al_2O_3.

In addition, an unprocessed DSP silicon wafer and a c-plane DSP sapphire wafer were coated with 10 nm NbN as a reference. Absorption (A) was estimated as $A = 1 - T - R$, where T and R are transmission and reflection respectively. Both transmission and reflection were measured in a UV-Vis-NIR spectrophotometer. To measure reflection at the desired wavelengths, an integrating sphere was used; the lining of the integrating sphere was composed of spectralon.

III. Results

The absorption of DSP silicon and DSP sapphire with and without 10 nm of ALD NbN is presented for reference in Figure 2. For the NbN coated samples the absorption increases to just over 50% in the near infrared range (1100–2500 nm). For NbN-coated sapphire, the absorption is constant at ~55% when continuing to the near-UV range. Notably for NbN-coated DSP silicon, absorption *decreases* in the visible region. This can be explained by NbN being more reflective than Si in this region. [15], [27]

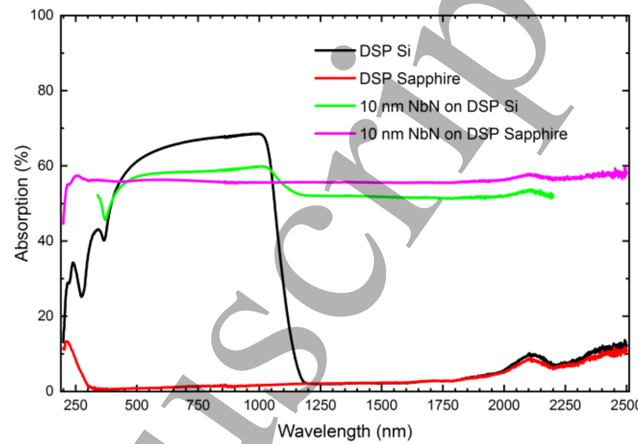

Fig. 2 Absorption spectra of DSP silicon and DSP sapphire with and without a 10 nm ALD NbN layer.

Figure 3 presents the absorption spectra for uncoated b-Si, b-Si coated with ALD NbN with a thickness of 10 or 15 nm, b-Si coated with ALD NbN with a thickness of 15 nm nanostructured by n-Al_2O_3 intermediate layer with as-deposited thickness of 5 or 10 nm, and uncoated DSP silicon for reference.

As can be seen, efficient suppression of reflection in the UV-visible region is achieved with the b-Si. However, in the NIR region (1200–2500 nm) the texturing is ineffectual at significantly increasing absorption and b-Si has similar absorption as DSP silicon. The b-Si coated with NbN has dramatically improved absorption in the near infrared region. With 15 nm of ALD NbN absorption of ≥99% extends over the broad spectral region of 200–1800 nm range. In the NIR region absorption steadily decreases and reaches a minimum at 2500 nm of ~94% and ~97% for the 10 and 15 nm thick NbN coated b-Si respectively. In the UV region an enhancement in absorption is also noted. No appreciable difference in absorption between the 10 and 15 nm thick NbN coatings is observed in the UV-visible spectral region up to 1050 nm wavelength.

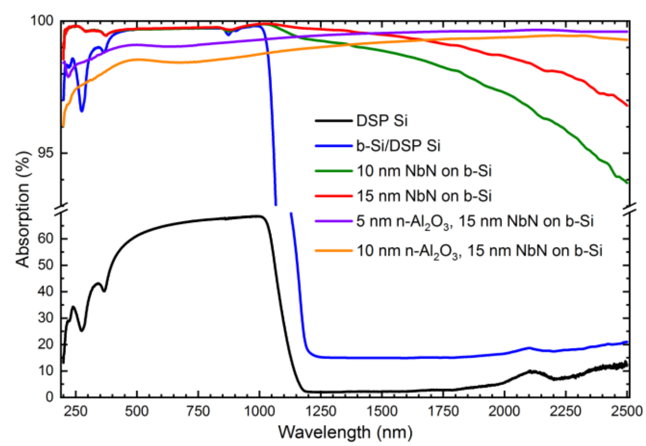

Fig. 3 Absorption spectra for uncoated b-Si, b-Si coated with 10 nm and 15 nm of ALD NbN, and b-Si coated 5 nm and 10 nm (as deposited

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thicknesses) of ALD n-Al_2O_3 and 15 nm of ALD NbN. Absorption spectra of DSP silicon is included for comparison. All the absorption spectra except DSP Si were smoothed in 'OriginPro 2016' software to reduce the noise in measurement results due to low intensity of the transmitted and reflected light.

The samples with nanostructured NbN films showed even higher absorption in the NIR region. With as-deposited 5 nm of n-Al_2O_3 and 15 nm of ALD NbN absorption >99% throughout the NIR region is achieved. Contrary to the films without the grass-like alumina intermediate layer absorption spectra demonstrates a steady increase further in the IR saturating at ~99.6% after ~1300 nm. However, as the grass-like alumina layer provides higher surface area for NbN deposition, higher mass of NbN per substrate area is deposited, which leads to increased reflectance in the UV-visible range of spectra, hence a slight underperformance in this region compared to b-Si with only NbN coating. Nonetheless, absorption in the visible region remains above 98.5% dropping down to only 98% in the UV region for the films with 5 nm of grass-like Al_2O_3. Increasing the thickness of grass-like Al_2O_3 did not produce higher absorption in any measured region of the spectrum showing on average ~99.3% absorption in NIR range and ~98% in UV-visible range.

The enhancement in absorption by nanostructuring with pre-deposited grass-like alumina opens new possibilities for various applications, as the resulting structure can be under 50 nm in thickness, while having massive surface area. Nanostructured NbN can potentially be utilized in other structures and metamaterials, like plasmonic nanoantennas [28], [29], to alter or improve sensitivity of the systems. Additionally, it is possible to combine nanostructured NbN not only with black silicon prepared by RIE but also with porous silicon prepared by various chemical methods [11]; to do that thinner Al_2O_3 and NbN should be used. However, more investigation into absorption mechanisms of nanostructured NbN should be conducted.

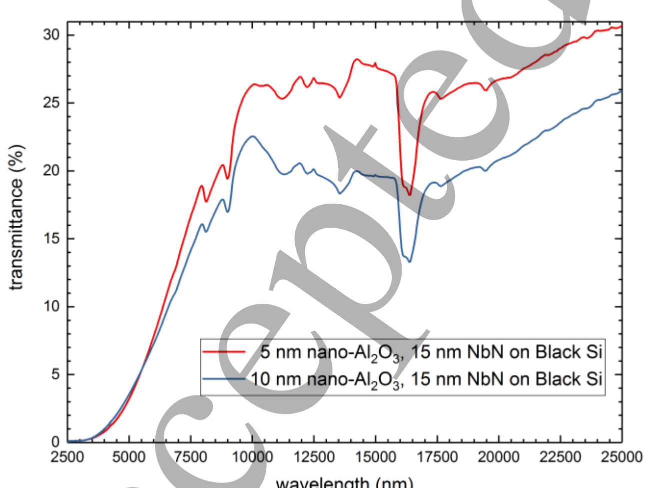

Fig. 4 Transmittance spectra for b-Si coated with nanostructured NbN films measured with an FTIR equipment.

Transmittance at wavelengths region from 2.5 µm to 25 µm of the NbN coated b-Si samples containing a nanostructured Al_2O_3 intermediate layer was estimated using a Fourier Transform Infrared Spectroscopy (FTIR) equipment, the measured spectra are in Figure 4. Transmittance appeared to stay below 1% for wavelengths below 4 µm indicating high absorption and achieved 5% only at about 5.5 µm. For comparison, in 2013 silicon chalcogen-hyperdoped and nanostructured via femtosecond laser achieved absorption of ~92–95% in the range 850–1000 nm and ~85% in 1–6 µm [7]. Black silicon with nanostructured NbN outperforms these absorption levels. Such high absorption over broad wavelength range is a desired feature for bolometer applications [30].

The difference in transmittance level at wavelengths above 10 µm is caused by the difference in the amount of NbN deposited on 5 nm and 10 nm Al_2O_3. 10 nm of Al_2O_3 provides higher surface area and allows higher mass of NbN per substrate area being deposited, compared to 5 nm of Al_2O_3. The used technique does not provide precise values of absorption, but indicates the tendencies in absorption behavior, implying that the measured samples work as strong absorbers in IR up to about 4–5 µm.

IV. Conclusions

Dramatically increasing the absorption of b-Si in the near infrared region is made possible by depositing a thin, 10–15 nm, layer of ALD NbN. B-Si coated with NbN exhibits much enhanced absorption in the near infrared region and UV region compared to plain b-Si. High absorption of 99–97% is achieved in the spectral region of 1100–2500 nm with a 15 nm layer of NbN. DSP silicon coated with NbN exhibits an absorption of only ~50% indicating a synergetic mechanism for absorption based on the microstructure of b-Si and NbN. Substantially increasing the surface area of NbN film by introducing an intermediate layer of grass-like alumina leads to a further improvement of absorption in the NIR region. Depositing 10 nm of grass-like alumina on b-Si and 15 nm of NbN on the top provides the absorption of 98–99% in the UV-visible range and continuous ~99.5% above 1300 nm without any decrease up to 2500 nm, and transmittance below 1% at wavelengths as high as 4000 nm. The used technique provides a significant improvement in wide-band absorption compared to silicon nanostructured by femtosecond laser [6]–[8] or chemically etched porous silicon [9], [12]. High absorption extend deeper into infrared region than reported results for a similar technique of coating b-Si with pyrolytic carbon [14]. The wide-band absorption of modified b-Si presented in this work indicates that NbN-coated b-Si is an attractive candidate for use in spectroscopic systems, heat dissipaters, infrared microbolometers and other thermal imaging devices thus warranting further study. In addition, the presented method of applying nanostructured Al_2O_3 and ALD NbN potentially can be utilized to enhance absorption of other previously developed structures and metamaterials.

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