Black Silicon nanostructures on silicon thin films prepared by reactive ion etching

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In this letter, the application of dry etching to prepare Black Silicon nanostructures on crystalline silicon thin films on glass is described. The utilized reactive ion etching with an inductively coupled plasma (ICP-RIE) of SF_6 and O_2 is discussed and a remarkable increase in light absorption of about 70% is demonstrated.

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Monolithic silicon nanostructures are able to greatly enhance the optical performance of silicon. Cost-efficient, self-organized fabrication methods of such Si nanostructures usually result in stochastic conical or needle-like structures, often referred to as "Black Silicon". When properly optimized, these implement an effective medium antireflection coating working over a large spectral range, even nearly independent on the angle of incidence (Fig. 1). Additionally, the Si nanostructures can scatter the incoming light into higher angles. This increases the optical path length within the underlying silicon absorber and even gives rise to multiple round-trips due to total reflection at the rear interface. Hence the overall light absorption is strongly raised, especially at higher wavelengths where the absorption coefficient α of silicon is small[1].

Nowadays, there are at least three well-established methods to fabricate Black Silicon structures reliably: repeated pulsed laser irradiation[2−4], wet-chemical etching[5,6], and inductively coupled plasma reactive ion etching (ICP-RIE)[7,8]. While the first two processes suffer from the formation of a defective surface area or chemical contamination, the latter dry etching method seems to be the most promising technique. It maintains the substrate's crystallinity and results in a chemically clean surface. Moreover, this method is easily adapted to existing manufacturing chains and is up-scalable, making it a mature technology with regard to an industrial application.

The potential applications of Black Silicon result directly from its characteristic properties, i.e., structure morphology and optical behaviour. The huge specific surface area makes it interesting for chemical sensors[9,10] or for energy storage, for example lithium batteries with increased capacity and load speed[11]. The high absorptance makes it ideal for optoelectronic sensors[12], solar cells[8,13], or thermoelectric power generation[14]. Furthermore, applications like photoelectrochemical water splitting could benefit from both properties[15].

Unfortunately, the ICP-RIE structuring method has not yet been established for silicon thin films so far, although this would be highly desirable for many of the named applications. In this letter, we show that it is possible to transfer the ICP-RIE method to silicon thin films and which problems may occur when doing so.

Black Silicon nanostructures were prepared both on double-side polished (DSP) Si wafers and on crystalline silicon (c-Si) thin films by ICP-RIE. For the latter, 10 μm of amorphous silicon (a-Si) were deposited on fused silica substrates using high rate electron beam evaporation. Then, the samples where crystallized via solid-phase crystallization in a furnace at 600 °C. Potentially appearing cracks in the crystallized Si layer, resulting from the higher thermal contraction of the film with respect to the substrate, did not affect the ICP-RIE structuring process.

Structuring is conducted in an ICP-RIE plasma etcher (SI 500C, Sentech Instruments). The inductive coupling ensures a low self bias and therefore low substrate damage. An additional bias voltage can be applied. As etching species only sulphur hexafluoride (SF_6) and oxygen (O_2) were used.

Substrate cooling is achieved by a simple cooling circuit, freezing the substrate holder down to about −49 °C. Thermal coupling between the holder and the substrate

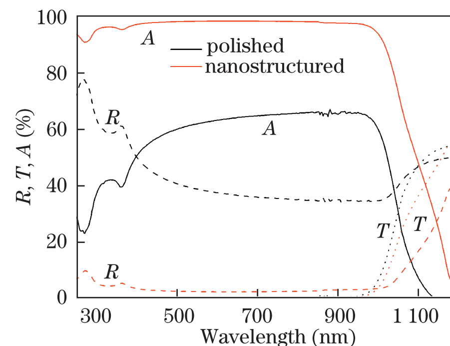

Fig. 1. (Color online) Reflectance, transmittance, and absorptance spectra of polished and Black Silicon nanostructured wafers.

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is delivered by gaseous helium. In the case of thin films on glass, samples were placed on silicon dummy wafers which were clamped into the substrate holder. Here, an additional thermal coupling between the substrate and the dummy was provided by placing a droplet of heat-conducting, synthetic oil underneath the sample.

Structure formation during ICP-RIE relies on random micro-masking by silicon oxyfluoride (SiO_xF_y) formed at the silicon surface and on reactive ion etching by fluorine radicals (F^*) in the plasma[7]. The combination of both effects results in specific nanostructures (Fig. 2) where the concrete geometry depends on the chosen etching parameters[1,8,16]. This means that the geometry properties like needle height and separation, as well as needle sidewall angles can be adjusted by an appropriate etching parameter variation.

However, due to strong decomposition of SiO_xF_y at elevated temperatures, the nanostructuring behaviour will get lost if the substrate temperature becomes too high. Since the substrate is continuously heated by a process-related ion bombardement, counter-cooling becomes necessary to achieve sufficiently low substrate temperatures.

For the silicon thin films on glass in this study, this issue appears pronounced due to the rather bad thermal contact between the glass substrate and the underlying silicon dummy wafer. This is well illustrated by the photograph in Fig. 3. In the black region ("1"), a sufficient thermal contact and hence counter-cooling was realized by a droplet of heat conducting oil between the glass and the dummy. On the other hand, in the shinier region ("2"), no oil spread beneath the sample and homogenous etching occurred rather than the desired nanostructuring.

Of course, the more sophisticated solution of the cooling problem is to use customized sample holders which provide direct thermal contact to the cold He gas instead of making a long way around by the use of an underlying silicon wafer.

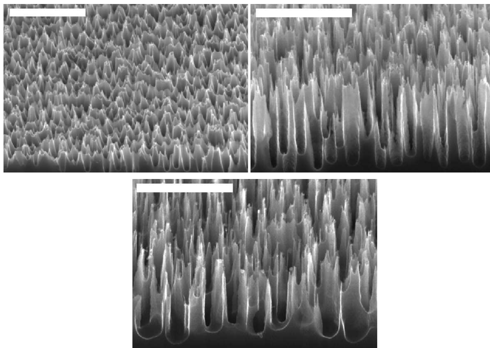

Fig. 2. Black Silicon nanostructures obtained under different parameters. The scale bars denotes 2 μm.

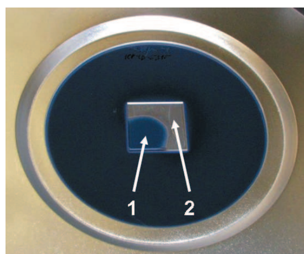

Fig. 3. Photograph of a partially nanostructured silicon thin film.

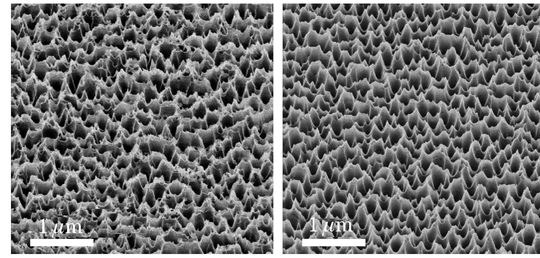

Fig. 4. Black Silicon nanostructure on thin film (left) and wafer (right).

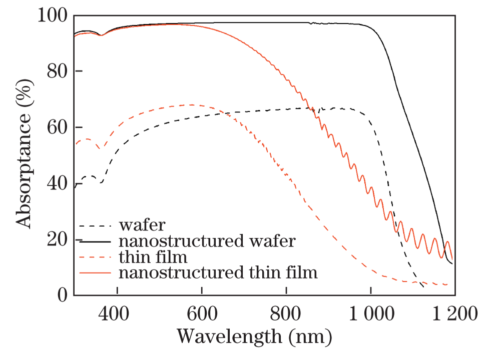

Fig. 5. Absorptance spectra of unstructured and Black Silicon nanostructured wafers and thin films.

The second important result is that if a sufficient cooling is somehow achieved, the nanostructures obtained on silicon thin films are basically identical to the structures obtained on wafers under the same parameters (Fig. 4). From the practical point of view, this is a notable result since it allows transferring wafer-optimized ICP-RIE recipes directly to silicon thin films on glass, hence shortening the corresponding developmental period greatly.

A typical absorptance spectrum of a Black Silicon nanostructured thin film is shown in Fig. 5. For comparison, also the spectra of the unstructured film as well as the spectra of a polished and a structured wafer are displayed. In the short wavelength region, the absorptance of the nanostructured thin film is comparable to the absorptance of the Black Silicon wafer. At longer wavelengths, the film is too thin to absorb the entire incident light, leading to a decreased absorptance with respect to the Black Silicon wafer. However, generally the absorpance is strongly increased compared to the unstructured film. Like stated before, this can be understood as a result of both the antireflection effect and the light scattering into higher angles of incidence.

Quantitatively speaking, the relative increase in absorptance amounts to 70%, which can be rightly called an impressively high value.

In conclusion, the transfer of the ICP-RIE Black Silicon method from wafers to crystalline silicon thin films on glass is demonstrated. Particular attention is paid to the sample counter-cooling, which reveals to be a necessary precondition for a successful Black Silicon nanostructure formation. It is shown that-sufficient cooling presupposed-the obtained nanostructures on silicon thin films equal their counterparts on silicon wafers and lead to a tremendous relative increase in absorptance of 70% in the case of a 10-μm-thick crystalline silicon film.

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References

1. M. Kroll, T. Käsebier, M. Otto, R. Salzer, R. Wehrspohn, E.-B. Kley, A. Tünnermann, and T. Pertsch, Proc. SPIE **7725,** 772505 (2010).
2. J. E. Rothenberg and R. Kelly, Nucl. Instrum. Meth. Phys. Res. B **1,** 291 (1984).
3. B. N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, and A. Tünnermann, Appl. Phys. A **63,** 109 (1996).
4. B. R. Tull, J. E. Carey, E. Mazur, J. McDonald, and S. M. Yalisove, MRS Bull. **31,** 626 (2006).
5. D. Dimova-Malinovska, M. Sendova-Vassileva, N. Tzenov, and M. Kamenova, Thin Solid Films **297,** 9 (1997).
6. Z. Huang, N. Geyer, P. Werner, J. de Boor, and U. Gösele, Adv. Mater. **23,** 285 (2011).
7. H. Jansen, M. de Boer, R. Legtenberg, and M. Elwenspoek, J. Micromech. Microeng. **5,** 115 (1995).
8. K. Füchsel, U. Schulz, N. Kaiser, E.-B. Kley, and A. Tünnermann, Proc. SPIE **7725,** 772502 (2010).
9. M. Archer, M. Christophersen, and P. M. Fauchet, Sensors Actuat. B Chem. **106,** 347 (2005).
10. J. Mizsei, Thin Solid Films **515,** 8310 (2007).
11. C. K. Chan, H. Peng, G. Liu, K. McIlwrath, X. F. Zhang, R. A. Huggins, and Y. Cui, Nat. Nanotechnol. **3,** 31 (2008).
12. Z. Li, B. K. Nayak, V. V. Iyengar, D. McIntosh, Q. Zhou, M. C. Gupta, and J. C. Campbell, Appl. Opt. **50,** 2508 (2011).
13. G. B. Jia, M. Steglich, I. Sill, and F. Falk, Sol. Energ. Mat. Sol. C **96,** 226 (2012).
14. A. I. Boukai, Y.Bunimovich, J. Tahir-Kheli, J.-K. Yu, W. A. Goddard III, and J. R. Heath, Nature **451,** 169 (2008).
15. X. Ao, X. Tong, D. S. Kim, L. Zhang, M. Knez, F. Müller, S. He, and V. Schmidt, Appl. Phys. Lett. **101,** 111901 (2012).
16. M. Kroll, M. Otto, T. Käsebier, K. Füchsel, R. Wehrspohn, E.-B. Kley, A. Tünnermann, and T. Pertsch, Proc. SPIE **8438,** 843817 (2012).