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Transfer of Heteroepitaxial Grown 3C-SiC Layers for Application in Optical Frequency Combs

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Abstract. We developed a process for the fabrication of SiCOI stacks which are a suitable platform for optical devices. Starting from 3C-on-Si samples the silicon substrate was removed by wet chemical etching and the remaining 3C-SiC layers were bonded to two different low refractive substrates (Al_2O_3 and polycrystalline SiC with a 3 µm thick SiO_2 layer on top deposited by PECVD). We found that also bonding onto Al_2O_3 was possible, the stability of the resulting stack wasn´t strong enough for further processing. In contrast mechanical stable SiCOI stacks could be realized using the oxide coated polycrystalline SiC as substrate. Besides the substrate materials three different bonding approaches (hydrophilic, hydrophobic and adhesive bonding using an HSQ resist) as well as multiple process parameters were analyzed with regard to the bonding performance. The best results could be achieved using the adhesive bonding approach with a bonding temperature ≥ 400°C, a process time ≥ 4 h and a bonding pressure of 96 N/cm^2.

Introduction

Silicon carbide (SiC) has been widely investigated for power electronic devices due to its wide bandgap, high breakdown voltage and high thermal conductivity. Besides SiC has become a material of interest for a variety of optoelectronic and photonic applications. Point defects (i.e. vacancies) in SiC can be used for quantum optical applications [1]. Based on the high refractive index (~ 2.6) and large indirect bandgap (> 2.3 eV) optoelectronic devices for a wide range of wavelengths can be realized using SiC. Furthermore, the high nonlinear optical behavior allows the fabrication of low-loss waveguides and high quality-factor (Q) microcavities for nonlinear photonic devices such as frequency combs [2, 3]. Among the most common SiC polytypes the cubic polytype (3C-SiC) is the only one that can be grown on a silicon (Si) substrate using epitaxial methods and allowing the integration with electronic devices. However due to the high diffraction coefficient of silicon an elaborate material processing is necessary to reduce optical losses at the 3C-SiC/Si interface such as undercutting of the silicon substrate [4]. A possible alternative is the fabrication of a SiC-on-insulator (SiCOI) stack using a low refractive material such as silicon dioxide (SiO_2). Different approaches to form SiCOI were presented in literature using smart cut methods of hexagonal SiC [5] or processes including high temperature oxidation of 3C-SiC [6] each suffering from different setbacks. A very promising approach was presented by Fan et al. [2]. They manufactured a SiCOI system by hydrophilic bonding of a 3C-SiC-on-Si and SiO_2-on-Si sample followed by removal of the top silicon layer which yielded Qs as high as 142,000 in a microring resonator fabricated in the 3C-SiC layer.

We developed a different process for the realization of SiCOI platforms. The process included the transfer of 3C-SiC thin films grown on silicon, the removal of this silicon substrate and bonding of the remaining 3C-SiC layer to a low refractive substrate. For the bonding three different techniques were tested and evaluated with respect to their performance. Additionally, the influence of different process parameters, e.g. temperature or bonding pressure will be presented and discussed in the following.

Materials and Methods

The starting point for the fabrication of the SiCOI platform were 3C-SiC thin films with a thickness of 10 – 20 µm grown by heteroepitaxial CVD on (100) orientated silicon and were provided by the company *NovaSiC*. The received 100 mm wafers were separated into smaller pieces using a laser ablation process. Consequently, the silicon was removed by wet chemical etching with a HNA solution consisting of HF (40 %) : HNO_3 (65 %) : H_2O in a ratio of 1 : 1 : 1.5. For handling of the samples, a self-made PTFE holder was used. After the etching the 3C-SiC layers were rinsed in deionized water and dried under a nitrogen stream. Sapphire (Al_2O_3) and polycrystalline SiC with a 3 µm thick SiO_2 layer on top (SiO_2-on-SiC) were used as low refractive substrates for the bonding process. The oxide on the SiO_2-on-SiC pieces was deposited by plasma-enhanced chemical vapor deposition (PECVD). Both substrates had a surface roughness below 1 nm. The substrates were cut into 2.5x2.5 cm^2 pieces using a wire saw. After the sawing they were cleaned in Acetone and Ethanol at 80°C for 10 min each, rinsed in deionized water and dried cleaned with a nitrogen stream.

For hydrophobic bonding the substrates were dipped in a buffered HF solution for 2 min. The 3C-SiC layers weren´t treated further as they already showed hydrophobic surface due to the HF containing etching solution used for the silicon removal. In case of hydrophilic bonding both the free-standing 3C-SiC layers and the substrates were treated for 15 min in an UV/Ozon furnace for surface activation. The success of the pretreatment was controlled by droplet test. For the adhesive bonding the substrates were pretreated for 15 min in a UV/Ozon furnace and afterwards spin coated with a hydrogen silsesquioxane (HSQ) resist. The surface activation was applied to increase the adhesion of the resist on the substrate material. The resist was made with HSQ powder and methyl isobutyl ketone (MIBK) as solvent from the company *EM Resist Ltd* with customized dilutions ranging from 6 – 12.5 %wt HSQ resulting in a layer thickness between 220 – 450 nm. The samples were placed on a hotplate for 2 min at 150°C and additionally for 1 min at 200°C to drive out the solvent. After the pretreatment the substrate and the 3C-SiC layers were brought in contact with the former 3C-SiC CVD front facing towards the substrate and placed in a self-build bonding machine. The setup could be heated up to 450°C, had a pneumatic cylinder which could apply a force up to 600 N and was able to operate under vacuum conditions. Table 1 gives an overview of the used process parameters.

Table 1: Overview of bonding parameters

Temperature	**Pressure**	**Atmosphere**	**Duration**	**Thickness of HSQ Resist** (only for adhesive bonding)
200 – 450°C	0.5 – 96 N/cm^2	Air, Vacuum	1 – 8 h	200 – 600 nm

Results and Discussion

Choice of substrate material. A suitable substrate material for the fabrication of SiCOI stacks has to have a lower refractive index compared to the active layer to minimize the optical losses of devices. This could either be achieved if a low refractive volume material is used or if a low refractive layer is added onto an otherwise optical dense material to decouple the substrate and the active layer. For the latter case SiO_2 is often used as it is relatively easy to deposited, e.g. by PECVD. In our study we tried both routes described and used Al_2O_3 and SiO_2-on-SiC as substrate materials. Figure 1 shows a comparison of a 20 µm thick 3C-SiC layers transferred to an Al_2O_3 substrate (Fig. 1a) and a SiO_2-on-SiC (Fig 1b) using the adhesive bonding approach. Also, the transfer was possible onto both substrates, for Al_2O_3 the 3C-SiC layer often appeared to be wavy/blister-like. The bonding strength was quite weak, independent of the used parameter set and bonding approach (see next section) and as a result the 3C-SiC could be removed easly with a tweezer. Additionally, bonding to Al_2O_3 proved to be chemical unstable during an RCA cleaning step. As RCA cleaning is a standard process during the manufacturing of optical devices Al_2O_3 seems to be unsuitable as substrate material for the fabrication of SiCOI stacks. In contrast no such behavior could be observed on the SiO_2-on-SiC

substrate. Here we found the 3C-SiC film to be homogenously bonded to the substrate and RCA cleaning didn´t result in removal of the 3C-SiC top layer. We assume that the weak bonding onto Al_2O_3 could be related to the difference in the coefficient of thermal expansion between Al_2O_3 and SiO_2/SiC. However, additional research needs to be done to better understand this observation.

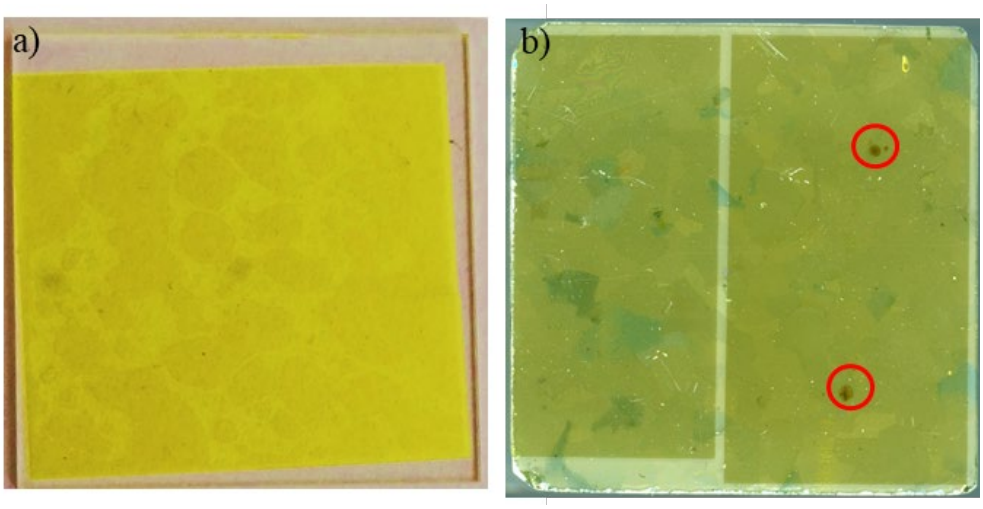

Figure 1: Top view images of 20 µm thick 3C-SiC layers bonded to a) Al_2O_3 and b) SiO_2-on-SiC substrate. For both samples and adhesive bonding approach with HSQ resist was used. The transferred layer on the Al_2O_3 appears to be wavy/blister-like while the layer on the SiO_2-on-SiC substrate shows good homogeneity. Two particles were trapped between the substrate and the 3C-SiC leading to a local burst of the top layer (marked with red circle).

Different bonding approaches. As mentioned in the materials section three different bonding approaches were tested in this study. The bonding approaches were tested for both Al_2O_3 and SiO_2-on-SiC substrates. However. for the Al_2O_3 substrate no stable bonding condition could be found independent of the used parameter set and bonding approach. Therefore, the following results are related exclusively to the experiments with SiO_2-on-SiC substrates. The substrates showed neither hydrophobic nor hydrophilic behavior after the oxide deposition (see Figure 2 a). For hydrophobic bonding the substrates were therefore dipped in a buffered HF solution while the etched 3C-SiC pieces already showed hydrophobic behavior after the silicon removal. However, using this hydrophobic bonding approach only weak attachment could be created between the 3C-SiC layers and the SiO_2-on-SiC substrates. The adhesion could be increased with increased bonding temperature, bonding duration and the application of a vacuum atmosphere. Nevertheless, the 3C-SiC top layer could be easily removed with a tweezer for all tested bonding parameters.

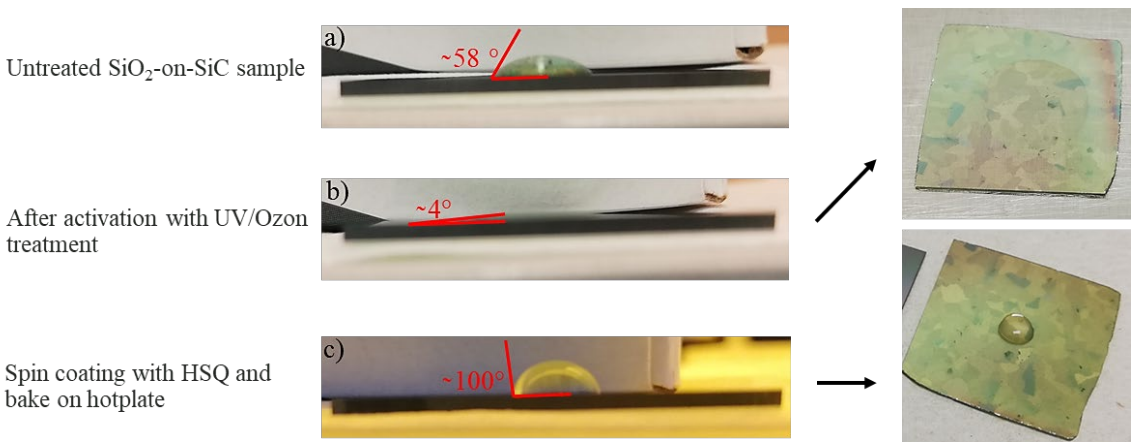

Figure 2: Effect of different treatments on the surface behavior of SiO_2-on-SiC substrates. a) untreated sample after the deposition of SiO_2 with PECVD, b) after surface activation with a UV/Ozon furnace, c) after application of HSQ resist and baking step to remove the solvent from the resist layer.

For the hydrophilic approach the substrates and the thin 3C-SiC layers were treated 15 min in an UV/Ozon furnace which resulted in a clearly visible hydrophilic surface (see Figure 2b). Tests showed that the UV/Ozon treatment had the same effect as a bath in piranha's acid (H_2SO_4 : H_2O_2 with ration 1 : 1) for 2 min. The biggest advantage of the UV/Ozon compared to wet chemical method is the simpler handling of samples which makes it ideal for the treatment of the fragile 3C-SiC thin films. The hydrophilic bonding resulted in a better adhesion compared to the hydrophobic approach. However again the 3C-SiC top layer could be removed after the bonding experiments once a slight force was applied to the sample. For both, hydrophobic and hydrophilic bonding, a further increase in bonding temperature, e.g. with a post bonding annealing step, could help to improve the bonding strength as it is used in direct silicon bonding with temperatures up to 1000°C [7]. However, due to the difference in thermal expansion coefficients between SiO_2 and SiC the operating temperature could be limited. Fan et al. reported a reduced yield of approx. 20 % during a hydrophilic bonding process of SiO_2-on-Si and SiO_2-on-SiC-on-Si pieces if the bonding temperature is increased from 300°C to 400°C [2].

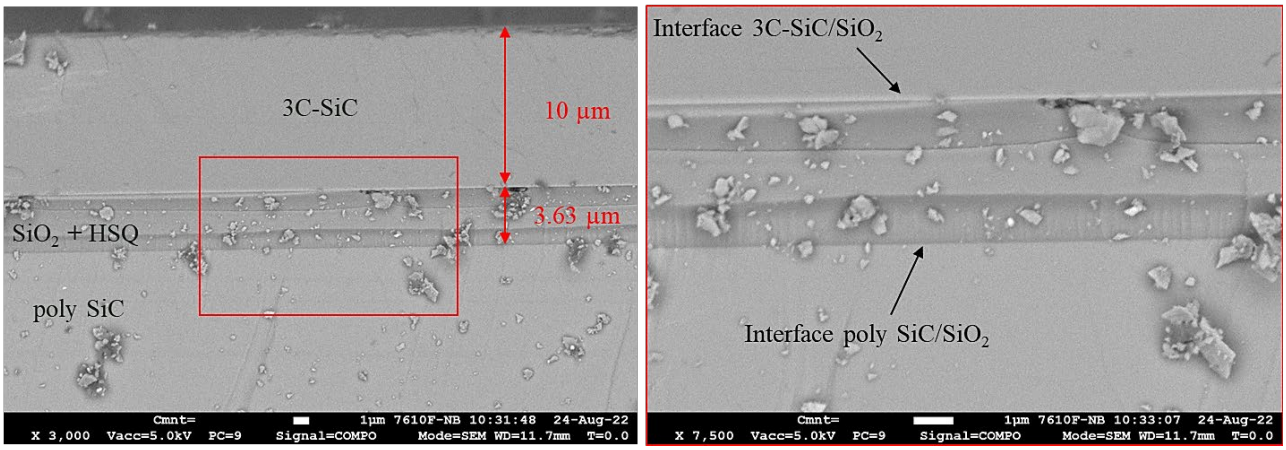

Figure 3: SEM images of a SiCOI stack crosscut after adhesive bonding with HSQ resist and high temperature annealing at 900°C. Clearly visible are the interface between 3C-SiC and the intermediate layer (PECVD deposited SiO_2 + HSQ) as well as the interface between the intermediate layer and the polycrystalline SiC underneath. No interface between HSQ and SiO_2 is visible indicating the formation of one continuous bulk like layer of SiO_2 responsible for the high bonding strength.

For the third bonding approach we added an HSQ resist as intermediate layer between the substrate and the 3C-SiC. HSQ is typically used in electron beam lithography but has already proven to be suitable for bonding of semiconductor materials [8]. The nontreated SiO_2-on-SiC substrate showed neither a hydrophobic nor hydrophilic surface. However, once the HSQ was spin-coated and the solvent removed by a bake step the surface got hydrophobic (see Figure 2c). After the bonding the two pieces (substrate and 3C-SiC layer) showed good adhesion if the temperature of the bonding process was ≥ 400°C. For lower temperatures the bonding strength was similar to the other two bonding approaches. Figure 3 shows scanning electron beam microscopy (SEM) images of a crosscut for a SiCOI stack fabricated with the adhesive bonding approach at 400°C. For this sample an additional annealing step at 900°C under argon atmosphere was performed after the bonding. The interface between the 3C-SiC top layer and the oxide intermediate layer is clearly visible as well as the interface between the oxide layer and the polycrystalline SiC underneath (see Figure 3 right-hand image). However, no such interface between the PECVD deposited SiO_2 and the HSQ resist can be observed. The average thickness of the PECVD deposited SiO_2 was measured to be 3.28 ± 0.054 µm compared to the thickness of the intermediate layer in Figure 3 which is 3.63 ± 0.004 µm. Based on the spin-coating curves the HSQ layer should have a thickness of approx. 450 nm. Taking into account the shrinkage of approx. 25 % for the HSQ during the annealing process [9] we expect a HSQ thickness of approx. 340 nm. Together with the PECVD deposited SiO_2 film this fits well with the observed thickness of the intermediate layer. While in [10] it is mentioned that for temperatures above

400°C the HSQ will transform into a porous SiO_2, for higher temperatures this porosity will decrease forming a dense layer of SiO_2 [11]. Therefore, we assume that the PECVD deposited SiO_2 and the HSQ resist form one bulk like SiO_2 intermediate layer during the bonding and annealing process which is responsible for the strong adhesion of the SiCOI stack.

Discussion of parameters for adhesive bonding. Besides the choice of substrate material, a series of additional parameters have a significant influence on the bonding result. As mentioned in the section before the temperature for the adhesive bonding has to be above 400°C in order to transform the HSQ resist into SiO_2. If the temperature is too low this process is non-complete or doesn´t work at all. As a consequence, bonding experiments at lower temperatures showed no or only insufficient bonding strength due to incomplete conversion of HSQ. A post bonding annealing step at elevated temperatures should increase the adhesion further due to a decrease of porosity in the transformed HSQ layer. In this context the process duration plays a crucial role as well. We observed an increased bonding strength if the process time was increased from 1 h up to 4 h. However, a further increase showed no significant influence. While Choi et al. [11] found that the transformation of HSQ was completed after approx. 1 h, the threshold for our experiments seems to be 4 h. The difference in the findings is most likely related with the increased HSQ layer thickness in our study compared to the 100 nm thin films in the case of Choi et al. We assume that the threshold time will be further increased for even thicker layers of HSQ which correlates with the results described in [9]. Additionally, we observed that the bonding strength increases for increased layer thickness of HSQ in the range tested in this study. Ryu et al. mentioned that thicknesses up to 1 µm can be used for bonding of GaN using HSQ [10]. The thicker layer helps to level out surface irregularities allowing the bonding of rougher surfaces and consequently reducing the necessary surface preparation prior to bonding. Besides temperature and layer thickness a higher bonding pressure is favorable to achieve an increased bonding strength. While bonding also worked for lower pressures (0.5 – 20 N/cm^2) the yield related to the successfully bonded surface area increased with increasing pressure during our experiments. Prior to the transformation into SiO_2 the HSQ is soft. For an increased pressure the soft HSQ molds better into the surface of the 3C-SiC top layer and the substrate, resulting in an increased homogeneity of the intermediate layer and consequently an increased adhesion after the bonding.

One final parameter of interest is the side of the 3C-SiC used for the bonding. The 3C-SiC layers used in this study were grown heteroepitaxial on silicon. Due to lattice mismatch and difference in thermal expansion coefficient of Si and 3C-SiC a high number of defects will be generated at the interface. This defect density can be strongly reduced with increasing 3C-SiC thicknesses. Using the CVD front side as contact surface in the bonding process has one main advantage compared to the side of the former interface. The transferred 3C-SiC layer has to be thinned down to approx. 500 nm in order to fabricate optical devices. If the interface side faces upwards after the bonding process the defective material gets removed and the remaining thin film has a high material quality. In contrast if the CVD side faces upwards the high-quality material will be removed during the thinning while the defect rich interface remains, which should lead to decreased device performance.

Outlook on thinning of 3C-SiC top layer. One remaining task is the thinning of the transferred 3C-SiC layer from the initial thickness down to approx. 500 nm. There are two possible routes to achieve this goal. Either dry etching processes with fluoride containing gases can be used or alternatively mechanical thinning with polishing or grinding can be applied. For dry etching the setup and process scheme can be complex, expensive and time consuming. Furthermore, the high operation powers necessary for the removal of SiC as well as the uniformity of the thin film thickness after the etching possess challenges to be solved. On the other, the bonding strength of the SiCOI stacks has to be high enough to withstand the mechanical shear forces applied onto the thin 3C-SiC layer during mechanical polishing. However, mechanical thinning opens up a cost-efficient and high throughput route for the fabrication of optical devices. First experiments on small scale (sample size 5x5 mm^2) showed that the SiCOI stacks fabricated with adhesive bonding were stable enough to thin down the 3C-SiC to approx. 5 µm using a polishing process established in our labs with a 6 µm diamond slurry.

However great attention has to be given to the mounting of the samples onto the polishing holder as the thin 3C-SiC layers will start to peel off if a wedge is formed during the polishing process.

Summary

We showed that it is possible to form a SiCOI stack starting from 3C-on-Si samples. The silicon was removed by wet chemical etching and the freestanding layer was bonded to a low refractive index substrate which is necessary for the fabrication of low loss optical devices. Although Al_2O_3 in theory is highly suitable as substrate material the bonding strength wasn't sufficient enough to enable further processing after the bonding. Using polycrystalline SiC with a top layer of SiO_2 deposited by PECVD as a substrate and HSQ resist as an intermediate layer between the substrate and 3C-SiC high bonding strength could be achieved. We found that the HSQ and the SiO_2 form one continuous, bulk like intermediate layer which we believe is the reason for the high bonding stability. Beside the temperature, the applied pressure as well as the process duration have a significant influence on the bonding strength. One remaining challenge is the thinning of the transferred 3C-SiC layer down to approx. 500 nm after the bonding process which is necessary for the fabrication of optical devices. First experiments using a polishing process to thin down the 3C-SiC top layer showed promising results. However further research and optimization is necessary on this topic.

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