Plasma roughening of polished SiC substrates

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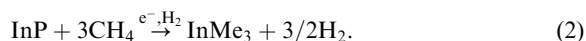
Abstract

Intended roughening of SiC can be performed in a one-step procedure (simultaneous generation and tear-off of a temporary mask) or in a two-step process which is far easier to control. A method is described based on the "contamination-induced" mechanism which allows reproducible roughening even of polished surfaces applying a parallel process. It makes use of a very thin layer of silver which is sputtered on top of the SiC surface and subsequently etched by means of a fluorine-containing high-density plasma generated by electron cyclotron resonance.
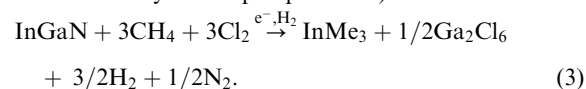© 2003 Elsevier Science Ltd. All rights reserved.

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1. Introduction

For several purposes, it is desirable to roughen surfaces of microelectronic devices to a certain, reproducible degree. With a roughened surface, the light output of LEDs can dramatically be increased [1,2]. Also, the efficiency of solar cells is improved. The active layers of blue-emitting LEDs: GaN, AlGaN and InGaN are patterned in aggressive plasmas containing chlorine [3,4]. Best results are obtained in a mixture of the four gases $Ar/Cl_2/H_2/CH_4$. With this ambient, it is possible to cover the whole range from pure GaN/GaAs (Ar/Cl_2) to pure InP (CH_4/H_2):

$$GaAs + Cl_2 + Cl \cdot \xrightarrow{e^-} 1/2Ga_2Cl_6 + 1/4As_4, \qquad (1)$$

$$InP + 3CH_4 \xrightarrow{e^-,H_2} InMe_3 + 3/2H_2. \qquad (2)$$

Al and Ga both form volatile $IIICl_3$ and III_2Cl_6. The good performance of Eq. (2) is supposed to the formation of the volatile metalorganic vapor $InMe_3$ and NH_3 [3] which has lead to the assumption that this process is the reverse MOCVD process (InCl and $InCl_3$ both have very low vapor pressures):

$$InGaN + 3CH_4 + 3Cl_2 \xrightarrow{e^-,H_2} InMe_3 + 1/2Ga_2Cl_6$$
$$+ 3/2H_2 + 1/2N_2. \qquad (3)$$

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This chlorine-based ambients fail completely for patterning of SiC. Following Hong et al., F-based chemistries like SF_6, CF_4 or CHF_3 are well suited to obtain sufficient etch rates of approximately 1/2 μm/min across wafer diameters of 2 in [5]. As Steckl and Yih [6] pointed out, care must be taken to avoid micromasking, which is not only due to the mask material (they applied a layer of gold; the scattered residues can be detected only in close neighborhood of the mask) but also to etching of the electrode (mostly consisting of aluminum, then scattered across the whole sample). This effect, they found out, can effectively be suppressed adding hydrogen to the plasma.

In these cases, a clean surface is required. The methods to prove this are SEM and AFM. To roughen a smooth surface of SiC reproducibly, remains a challenge. This problem arises when the light output of a GaN-based LED shall be increased by technological means. As we have shown, it is feasible to enhance the efficiency of a blue-emitting diode by a factor of 2 when the four sidewalls (SiC) are roughened [7]. The isolated diodes which are glued bottom-down on an adhesive tape and which have their top contact covered with drops of photoresist, are etched in a high-density plasma consisting of $N_2/O_2/Cl_2/CF_4$. Since this is a single-diode process, it cannot be adopted by a process line. Therefore, a process is required which should be the first step of the processing. As the p-contact is extremely sensitive to any dry etching [8], the n-side remains as the

only possible surface to become roughened. The mask should resist as long as optical obstacles are completely developed, or the process should belong to the "contamination-induced" mechanism [9]. This mechanism requires a mask which will be created continuously during the whole etching process [10]. Furthermore, the grain size should be controlled not only by optical methods (SEM or AFM) but also by optical measurements in a reflecting sphere.

The temporary mask can be generated and attacked during the process; it is then continuously delivered (true "contamination-induced" process) or is eroded after having coined its structure sufficiently deep into the SiC. The first procedure requires a delicate equilibrium between deposition and etching which can be achieved e.g. by controlling the flow ratio between O_2 and SF_6, the second possibility makes use of a thin metal layer (less than 100 nm thick) which is coated atop the SiC. The withdrawal of the mask happens discontinuously thereby creating spots of micromasking material.

2. Experimental

Very thin layers ($\leqslant 100$ nm in thickness) of titanium, molybdenum, silver and tungsten are sputtered on SiC substrates. They are exposed to reactive plasmas (either capacitively coupled or generated by ECR) composed of SF_6/O_2, sometimes doped with Cl_2. The exact conditions for both the processes are given in the figure captions.

3. Results

Application of various metals has led us to the following conclusions:

- The layer can be very very thin, and must not be opaque (Ag: 50 Å $\leqslant d \leqslant 100$ Å).
- From the applied metals (titanium, molybdenum, silver and tungsten) silver has shown its superiority. We refer this mainly to the fact that all other metals will form volatile fluorides. For silver, this is definitely not the case [11]. Although this metal exhibits one of the highest sputter yields, this is dramatically decreased by doping the atmosphere of the discharge with fluorine. The formed AgF and AgF_2 are known to be extremely non-volatile, but decompose under UV radiation. Therefore, they will be in a dynamic equilibrium with Ag and F, but will remain sufficiently long to allow for fine interpenetrating cones and pyramides.
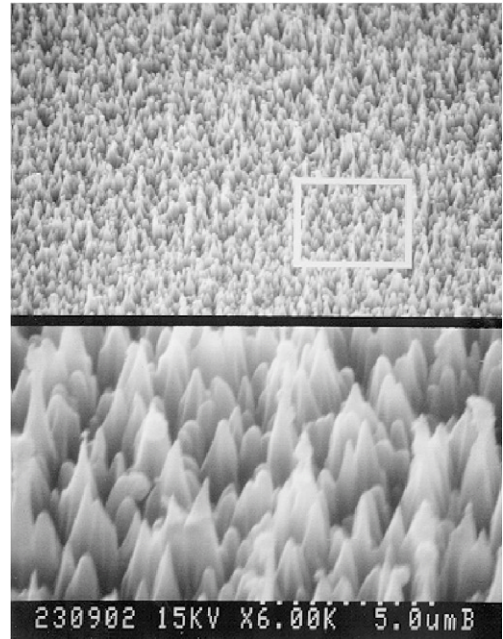- Therefore, additional doping with chlorine will not change this effect.

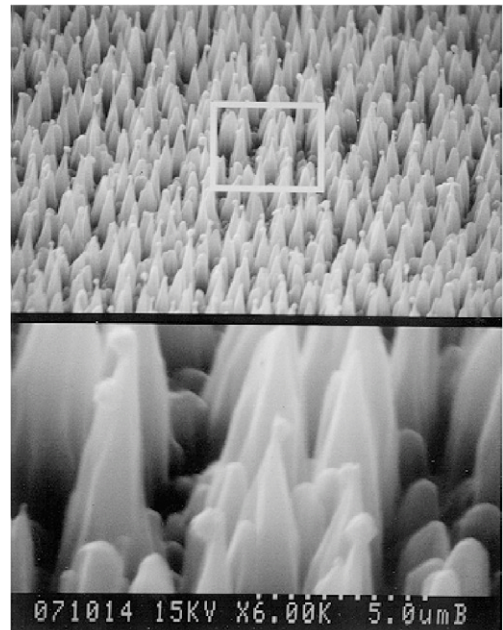Fig. 1. The surface has been roughened using the "contamination-induced" mechanism: 1st step: coating with a thin silver film sputtering conditions: Pre-etch with Ar: Flow: 1.6 sccm, p: 6 mTorr, P_{RF}: 200 W, t: 2 min, Coating: Flow: 1.6 sccm, p: 6 mTorr, P_{RF}: 50 W, V_{DC}: -400 V, t: 1 min, ECR conditions: P_{MW}: 600 W, P_{RF}: 50 W, V: -65 V, Ar : O_2 : $SF_6 = 10 : 5 : 20$, t: 33 min.

Fig. 2. Sputtering conditions: Pre-etch with Ar: Flow: 1.6 sccm, p: 6 mTorr, P_{RF}: 200 W, t: 2 min, Coating: Flow: 1.6 sccm, p: 6 mTorr, P_{RF}: 50 W, V_{DC}: -400 V, t: 1 min, ECR conditions: P_{MW}: 600 W, P_{RF}: 50 W, V_{DC}: -60 V, Ar : O_2 : $SF_6 = 10 : 5 : 20$, t: 34 min.
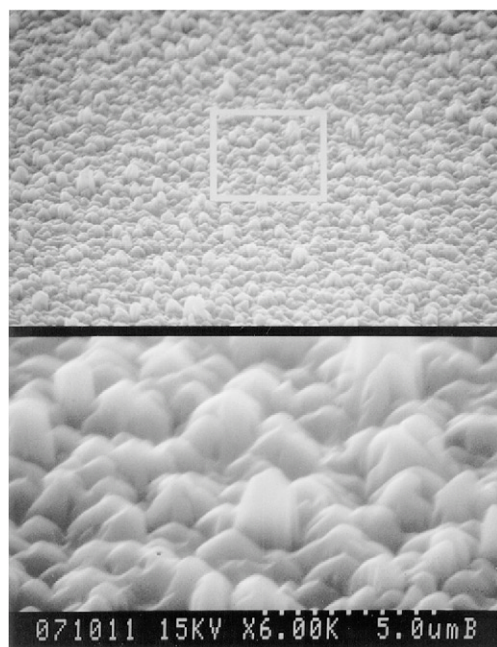
Fig. 3. The surface has been roughened using the "contamination-induced" mechanism: 1st step: coating with a thin silver film sputtering conditions: Pre-etch with Ar: Flow: 1.6 sccm, p: 6 mTorr, P_{RF}: 200 W, t: 2 min, Coating: Flow: 1.6 sccm, p: 6 mTorr, P_{RF}: 50 W, V_{DC}: −400 V, t: 1 min, ECR conditions: P_{MW}: 600 W, P_{RF}: 100 W, V: −121 V, Ar : O_2 : Cl_2 : SF_6 = 10 : 5 : 9 : 20, t: 20 min.

The structures generated in a high-density plasma driven by electron cyclotron resonance can be distinguished by the different metal layers. A three gas ambient of Ar, O_2 and SF_6 creates pyramides (Fig. 1, dc bias approx. −60 V) with silver, but needles with the other metals. This process is very reproducible, as shown in Fig. 2.

In a plasma consisting of four gases (Cl_2 is added), a very fine grain structure develops which reminds of crystallographic (wet) etching (Fig. 3).

The roughness can be easily adjusted by variation of the exposure time. As it is known from Carter's theory [12], acute cones and pyramides are the first state of surface roughening, which is gradually transformed into the second state when their shape is rounded. In the third state, broad, relatively flat tubs are generated. So the surface of Fig. 3 is closely connected to further development of surfaces in Figs. 1 and 2 by prolonging the exposure time by 30%. The optimum in roughness depends on the material wavelength. For the scattering of blue light in SiC, the roughness should be not larger than approximately 150 nm to meet the requirements. This is the base length of the pyramides in Figs. 1 and 2.

4. Conclusion

Surface roughening even of polished SiC substrates can reproducibly be performed applying a two-step process: in the first step, a temporary metal mask is coated which is subsequently etched either in a low-density plasma of a parallel-plate reactor or in the high-density plasma generated by electron cyclotron resonance. This method belongs to the class of the "contamination-induced" mechanism which allows reproducible roughening of polished SiC surfaces applying a parallel process. It is easily applicable and does not need individual handling of the separated devices.

References

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