***In situ* hole doping of wide-gap semiconductors by dual-target simultaneous laser ablation: GaN and SiC epitaxial films**

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Apparatus for dual-target simultaneous laser ablation deposition and *in situ* doping techniques have been developed to achieve *p*-type doping during epitaxial growth of wide-band-gap semiconductors. The apparatus has two target holders with a target-rotation mechanism and a rotation-axis adjusting mechanism to obtain homogeneously doped films. Mg-doped GaN films have been fabricated on 6H-SiC(0001) and Si(111) substrates in NH₃ ambient by simultaneous ablation of GaN and Mg-metal targets using two lasers. Junctions of the films with *n*-type substrates show a diode curve characteristic of *p-n* junctions, but not for junction with *p*-Si, indicating hole doping without further procedures. *In situ p*-type doping to SiC was also achieved by using SiC and Al₄C₃ targets. © 2005 American Institute of Physics. [DOI: 10.1063/1.2105989]

As well as GaN, both SiC and ZnO are expected to be next-generation semiconductors suitable for use in electro-optic fields, including the reduction of energy consumption.^{1–3} They have a wide band gap and good thermal stability originating from their very high melting or growth temperatures, respectively, 1700, ~2700, and 1970 °C.^{4,5} However, the high temperatures make the device processing difficult. In particular, a breakthrough is needed for *p*-type doping along with the fabrication of high-quality crystalline layers. Dopant atoms, such as B, Al, N, P, As, Mg, and Zn are introduced to the films by ion implantation or by adding their metalorganic (MO) compounds during film fabrication by chemical vapor deposition (CVD) or vapor phase epitaxy. The dopant atoms cannot migrate easily. The doping process also destroys the crystalline lattice or creates unwanted complexes with hydrogen atoms produced by the decomposition of MO. As a result, charge compensation occurs, with mobile electrons associating with the lattice imperfection. For GaN, the first success in *p*-type doping was made by Akazaki using low-energy electron-beam irradiation of the doped films.^{6,7} The breakthrough, together with clarification of the activation mechanism, was made by Nakamura^{8–12} using a sophisticated postprocedure of high-temperature annealing which made it possible to activate dopant atoms by the decomposition of Mg-hydrogen complexes after a sophisticated form of CVD called two-flow MOCVD. The SiC is doped by implantation of B or Al ions, or by adding their MO compounds in the CVD processing, which also need subsequent annealing at very high temperatures around 1500–1700 °C.³ Thus, *p*-type doping is still difficult, and alternative techniques that take only a single step at low temperatures are desirable. Using pulsed laser ablation deposition (PLAD), we have fabricated heteroepitaxial films of SiC.^{13–15} Polytypes, such as 2H, 4H, and 3C-SiC, were grown on sapphire and Si single-crystal substrates at low temperatures of 1200–1300 °C.^{15–17} PLAD has many advantages and is useful for fabricating other wide gap semi-

conductors, such as GaN,^{18–21} ZnO,^{22,23} and diamond,^{24,25} as well as superconductors,²⁶ ferroelectrics,²⁷ and magnetoresistance materials,²⁸ but apparatus and techniques for doping have not been developed. Doping might be possible with conventional apparatus using a single target if mixed targets are to be prepared. However, it is hard to sinter the mixed target of a wide gap semiconductor with a very high melting temperature and a dopant that has a low evaporating temperature.

We have devised a PLAD technique for achieving *in situ* hole doping, as shown in Fig. 1(a). We believe that doping becomes possible if the dual targets of film and dopant are ablated separately but simultaneously, even though they have very different melting temperatures and/or chemical stabilities. PLAD also provides processing without MO. The chamber is equipped with two target holders, 1 and 2, each of which can mount one target and has a motor-driven target rotation mechanism for homogeneous ablation and an *x-y*

FIG. 1. Dual-target simultaneous PLAD apparatus for *in situ* doping during film growth using a couple of targets and lasers (a), and RHEED pattern for (i) Mg-doped GaN film (b), and *I-V* curves observed for junctions of (i) Mg-doped and (ii) non-doped GaN films vs *n*-6H-SiC(0001) substrate (c). (a) The apparatus is equipped by two target holders with a motor-driven target rotation mechanism and an *x-y* stage.

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stage. The substrate is mounted on a heater at the counterposition of the targets. The targets are ablated by two laser beams (1 and 2) entering the chamber through optical windows. High-energy particles are ejected from the two targets and form plumes by laser irradiation. The plume directions are adjusted using the x - y stages so that both plumes just reach the center of the substrate and produce a homogeneously doped film. We used the fourth harmonic (266 nm) of two Nd:YAG lasers, a Spectron LS-803, and a LOTIS TII LS-2135, to ablate the film and dopant targets, respectively. The irradiation energy density (fluence: F) can be changed independently using lenses.

As targets for the films, we used sintered disks of GaN and 6H-SiC with a purity of 6N. p -type doping was attempted using Mg metal as the p -type dopant target for GaN, and using the four targets Al_4C_3 , B_6Si , B_4C , and Al metal for SiC. Their diameter is 20 mm ϕ . The dopant concentration in the films can be controlled by changing the relative values of the PLAD parameters for the film and doping targets: The energy E , fluence F , and repetition frequency f_p of the two lasers. It was found that the p -type films prepared at optimal conditions had the dopant concentration of about 2–3%. The concentration was estimated from the arriving (or growth) rates of the film and dopant materials which were obtained by individual PLAD for two targets on the assumption that all arrived dopant atoms on the substrates were involved in the films even in the case of dual-target simultaneous PLAD.

Optimal conditions for Mg-doped GaN films are: $E=50$ mJ/pulse, $F=1.0$ J/cm²/pulse, and $f_p=5$ Hz for the GaN target, and $E=25$ mJ/pulse, $F=1.0$ J/cm²/pulse, and $f_p=1/2$ Hz for the Mg target. The doped films were fabricated on n -6H-SiC (0001) and n or p -Si (111) substrates in an ammonia atmosphere at pressure $p=5$ Pa and heater temperature $T_h=700$ – 800 °C. Similar conditions were used for p -type doping of SiC, except for deposition in a vacuum ($p\sim 2\times 10^{-7}$ Pa) and at a high temperature of $T_h\sim 1200$ °C. The quality of the films and p - n junctions was examined by x-ray diffraction (XRD), reflection high-energy electron diffraction (RHEED), atomic force microscopy (AFM), and current-voltage (I - V) measurements.

XRD revealed that the Mg-doped GaN film grew with the same c -axis orientation as the substrate 6H-SiC. Apart from the substrate 6H-SiC (0006) and (00012) peaks, the XRD patterns showed only two XRD peaks, at $2\theta=34.84^\circ$ and 73.37° , which are assigned to (0002) and (0004) diffractions of hexagonal GaN. The lattice parameter estimated from the 2θ values ($c=0.515$ nm) agreed with that of GaN ($c=0.517$ nm).⁴ Epitaxial growth of the GaN film was confirmed by the RHEED patterns shown in Fig. 1(b), which is observed in the electron-beam direction parallel to the GaN [1-100] direction. The lattice size estimated from the line separation ($a=0.318\pm 0.002$ nm) agrees with the reported value for GaN ($a=0.3186$ nm).⁴

The I - V character observed for the junction of Mg-doped GaN film/(0001) n -6HSiC substrate is shown in Fig. 1(c) with filled circles. This displays a diode character due to the p - n junction, i.e., a low leak current in the reverse bias region up to -20 V, and a steep increase in current with the forward bias. These results clearly indicate the successful achievement of *in situ* p -type doping of GaN. The dead voltage at 4–5 V in the forward region is due to a Schottky barrier resulting from contact with a silver (Ag) metal electrode that we used for convenience. For reference, we fabri-

FIG. 2. I - V curves and RHEED patterns for film/substrate junctions. (a) Curves are observed for the epitaxial film of Mg-doped GaN fabricated on (i) n - and (ii) p -Si(111) substrates, and for (iii) polycrystalline Mg-doped GaN film fabricated on n -Si(111). (b) and (c) RHEED patterns for (i) epitaxial and (iii) polycrystalline films of Mg-doped GaN on n -Si, respectively.

cated nondoped GaN film on the n -6HSiC (0001) plane, which gives rise to an n -type film with n carriers due to intrinsic lattice defects. The I - V curve of the n / n junction is shown by the open squares in Fig. 1(c), which displays no diode character, but does have a Schottky nature showing a symmetry with respect to reverse of the bias, except for the polarity of I . This is mainly due to Schottky contact between film and metal electrode.

In situ p -type doping also takes place on other substrates. Figure 2(a) shows the I - V curves observed for junctions of epitaxial films of Mg-doped GaN which are fabricated on: (i) n and (ii) p -Si(111) substrates at $T_h=750$ °C and for (iii) polycrystalline Mg-doped film fabricated at $T_h=650$ °C on n -Si(111). Their epitaxial and polycrystalline growth are verified by RHEED as shown in Figs. 2(b) and 2(c) for (i) and (iii) films. A diode character is observed for the p -film/ n -substrate junction (i) (closed circles), but a nearly straight line is seen for the p - p junction (ii) (open squares). Surprisingly, a diode character was observed for junction (iii) of polycrystalline Mg-doped film/ n -Si (open circles), though the I - V quality was lower than that of the epitaxial films. These results imply that the present dual-target simultaneous PLAD causes the doping and activation of p -type dopant to occur readily in a single step without further processing.

The technique has also been applied to SiC, which is very hard to dope because of its extremely high growth temperature.³ We attempted *in situ* p -type doping of SiC using three kinds of sintered target (Al_4C_3 , B_4C , and B_6Si) and an Al metal target. Success was found only with Al_4C_3 . The I - V curve for the junction (i) between the film and n -6HSiC (0001) substrate is shown by closed circles in Fig. 3(a). A diode character is clearly observed. Other dopants result in I - V curves having nearly a Schottky nature, as shown with open triangles for a typical film fabricated on n -SiC using B_4C dopant target. For reference n -type-doped SiC film was fabricated on an n -SiC substrate using Si_3N_4 n -dopant target. The curve for the resulting junction is shown by the open squares. It is almost a straight line, characteristic of the n - n junction. It was found that the above p -type film had much lower surface roughness (root-mean-square ~ 1.0 nm) than the other films (2–5 nm), as shown in Figs. 3(b) and 3(c),

FIG. 3. I - V curves observed for junctions of *in situ*-doped SiC epitaxial film/*n*-6H-SiC substrate (a), and AFM images (b) and (c) for the SiC films fabricated by dual-target simultaneous PLAD using (i) Al_4C_3 and (ii) B_4C *p*-type dopant targets. The curve (iii) in (a) shows I - V character for an *n*-type film prepared using (iii) Si_3N_4 *n*-type dopant for reference.

while their crystallinity estimated from the full width at half maximum values of SiC(0006) XRD rocking curves did not differ largely from each other. These results suggest that the achievement in *p*-type doping needs growth of films with high crystalline quality including surface flatness, although the detail mechanism must be clarified.

We have developed a dual-target simultaneous PLAD apparatus and corresponding techniques, and studied *p*-type doping of wide gap semiconductors, such as GaN and SiC. Their successful *in situ* *p*-type doping on various substrates, such as Si and SiC, suggests a wide applicability of these techniques to hard materials that can be grown, in addition to other wide gap semiconductors, such as ZnO and diamond.

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