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Eradicated unintentional incorporated donor-type impurities of ZnO

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Impurity control is essential for semiconductor doping. Through the systematic analysis of pollution sources, we determined that the residual electrons of as-grown unintentional doped zinc oxide (ZnO) films were derived from the unintentional incorporation of silicon, which grown by molecular beam epitaxy. At the same time, it was determined that unforeseen donor-type impurities (boron, carbon, chlorine and fluorine) were introduced during the nitrogen doping process. By subjecting the sources of the contamination to a surface passivation process, these donor-type impurities are controlled at a tolerable level. The residual electrons concentration of the unintentional doped ZnO film was lowered to 1×10^{15} cm^{-3}, and the mobility was 155 cm^2/V·s. Nitrogen-doped ZnO films exhibited p-type conductivity, with a hole concentration of 2×10^{16} cm^{-3} and a mobility of 10 cm^2/V·s. Our results provide a pure foundation for further research on p-type doping of ZnO.
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I. INTRODUCTION

The desire for p-type zinc oxide (ZnO) has been a top priority for ZnO-based ultraviolet optoelectronics research.[1,2] We know that the premise of obtaining p-type ZnO is the effective doping. Furthermore, accurately controlling the incorporation of impurities or defects is the key to semiconductor doping. Up to now, many of the fundamental experimental issues about doping remain unresolved. Low residual carriers concentration is one of the vital basis for p-type doping of ZnO. Usually, unintentional doped ZnO films have a residual electrons concentration of about 1×10^{16} cm^{-3},[3–5] which indicating that there are more donors exist. Moreover, the origin of n-type conductive behavior of as-grown ZnO has not been conclusive. At first, the native point defects, zinc interstitials (Zn_i) and oxygen vacancies (V_O), were considered the donors of residual electrons.[6–8] However, according to the theoretical calculation and the experimental results,[9–11] the V_O are the deeper donors which can not effectively ionize, while the Zn_i have lower migration barrier, so that they are not stable at room temperature. Consequently, it is necessary to reanalyze the n-type conductivity of ZnO thin films based on experimental evidence. In general, in order to influence the conductivity of the semiconductor, the amount of impurities or defects in the order of one thousandth of the order, for wide bandgap semiconductor, even up to one percent of the order of magnitude.[12] Therefore, during the epitaxial growth of ZnO, there are must be some impurities which were neglected.

In this work, we systematically analyze possible sources of impurity elements. At the same time, by using secondary ion mass spectroscopy (SIMS), the type and content of impurities in the ZnO film grown by molecular beam epitaxy (MBE) were quantitatively analyzed. Finally, the

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unintentional incorporated donor-type impurities have been suppressed via pollution sources surface passivation.

II. EXPERIMENTAL DETAILS

Unintentional doped and nitrogen (N) doped ZnO films were grown in MBE system (Finland DCA P-600), which equipped with solid-source effusion cells for zinc (Zn) and oxford radio-frequency (RF) atom source (HD25, operating frequency of 13.56 MHz) for active O and N. Elemental Zn (7N grade), O_2 gas (6N5 grade) and N_2 gas (6N grade) were used as molecular beam sources. The purity of O_2 and N_2 was further increased to 9N grade by using the getters (SAES Pure Gas, Inc.). The inner wall of the piping that delivers the gas is secondary remelted (Valex, 316L). The overall inboard leakage rate of gas line is as low as 2×10^{-10} sccs. The ZnO films were grown on 2-in. c-sapphire with MgO/ZnO double buffer layer. More specific growth conditions can be seen elsewhere.[13] It should be mentioned, however, that the RF atom source operates by means of an electrical discharge created through the inductive coupling of an RF excitation coil. The gas was delivered to the electrical discharge space which surrounded by discharge tube (DT) and aperture plate (AP). The materials of DT and AP are usually silica (SiO_2 for O_2) or boron nitride (BN for N_2), which was likely to cause impurities incorporated during the epitaxy (see below for further discussion). Impurities profiles were measured by SIMS, using cesium 133 ($133Cs^+$) and O_2^+ as the primary ion beam (CAMECA IMS-7F). All of the target elements have been calibrated. Conductivity measurements (mobility and carrier concentration) were made in a standard Hall system (Lakeshore HMS7707).

III. RESULTS AND DISCUSSION

As mentioned above, the DT and AP of O_2 RF atom source, made from SiO_2, probably produces Si atoms with the electrical discharge, and then makes the ZnO pollution. The Si is a n-type dopant in ZnO, which can lead to a multielectron shallow donor level.[14,15] Moreover, in order to define the effect of substrate (aluminum diffusion) and sample manipulator (made from molybdenum and tantalum), impurities (Si, Al, Mo, Ta) had been measured. Figure 1 shows these impurities profiles of ZnO film grown under unintentional doped conditions. As can be seen from the results, the concentration of Si is about 2×10^{18} cm^{-3}, which evenly distributed throughout the epitaxy layer. It indicates that pollution, from DT and AP, is really exist. Fortunately, the Al atoms from substrate have no grievous diffusion, just take place in less than 10 nm, which cannot contribute to the conductivity of the films. Simultaneously, the concentrations of Mo and Ta are reaching to the detection limits, which indicates that there are no pollution from the manipulator. Thus, according to our experimental

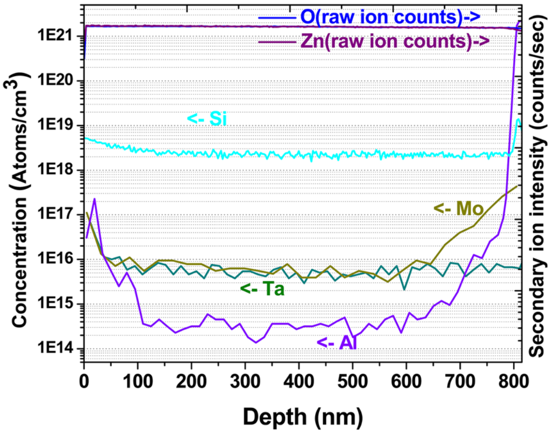

FIG. 1. The Si, Al, Ta and Mo depth profiles in unintentional doped ZnO films grown by molecular beam epitaxy.

evidence, the n-type conductivity of unintentional doped ZnO, residual electrons concentration of about 1×10^{16} cm^{-3}, can be explained by Si contamination.

To date, in many dopant, the N is considered the most suitable acceptor dopant. Although, based on some first-principles computational studies, the substitutional N doping on an O site (N_O) is a deep acceptor, which cannot give a p-type conductivity,[16] inconsistent, most successful p-n homojunction electroluminescence results have been realized by using N doping.[17–19] Moreover, some advanced theory models, N related defect-complex acceptors, have been developed, which could lower the acceptor ionization energy.[20–23] Therefore, N doping is still a challenge to be studied. To get the impurities profiles of N doped ZnO in details, SIMS has been utilized. As can be seen from the figure 2, just like Si contamination, the concentration of B, in N doped layer, is almost 1×10^{19} cm^{-3}, which indicates the pollution of DT and AP of N_2 RF atom source is also inevitable. In addition, there are some unforeseen donor-type impurities, carbon (C), chlorine (Cl), fluorine (F), have been found when N doping started. The Cl may be come from the precursor (BCl_3) of BN. The C and F may be come from the previous pollution, which be introduced during the synthesis process of BN. In short, the impurities (B, C, Cl, F) are come from DT and AP of BN, according to the SIMS results. The Si concentration was also measured. It is found to be constant in both of the layers (doped and undoped), with a value of $\sim 2 \times 10^{18}$ cm^{-3}, which is consistent with the unintentional doped samples. These donor-type impurities (Si, B, C, Cl, F) will inevitably become compensation centers for N, which in turn affect the efficiency of ZnO p-type doping.

In order to avoid the pollution of RF atom source, the DT and AP have been sputtered a ZnO passivation layer via RF ion sputtering. Sputtering target is made of ultra-high-pure zinc (7N grade) sheet. Subsequently, the DT and AT were annealed at 1000 °C under N_2 (6N grade) protection.

Figure 3 shows the impurities profiles of N doped ZnO by using the DT and AP with ZnO passivation layer. The concentrations of Cl (less than 10^{16} cm^{-3}) and F ($\sim 10^{15}$ cm^{-3}) are reaching their detection limits of the SIMS, respectively, which means that they can be considered no longer exist in ZnO. The Si, B, C concentration is also reduced significantly, with values of $\sim 1 \times 10^{17}$ cm^{-3}, $\sim 1 \times 10^{16}$ cm^{-3}, $\sim 5 \times 10^{16}$ cm^{-3}, respectively. Interestingly, the concentration of N is improved ($\sim 1 \times 10^{19}$ cm^{-3}) under the same conditions as previous N doping process. By utilizing the ZnO passivation layer, the undesirable impurities for p-type doping are reduced to the order of one ten thousandth or less, thereby reducing the influence of the compensation.

The conductivity of purified ZnO films has been measured by Hall with van der Pauw configuration at room temperature. Unintentional doped ZnO films exhibit higher resistivity (residual electrons concentration 1×10^{15} cm^{-3}, mobility 155 $cm^2/V \cdot s$), which further indicates the lower donor impurities levels. The hole conductivity has been detected in N doped ZnO films (hole concentration

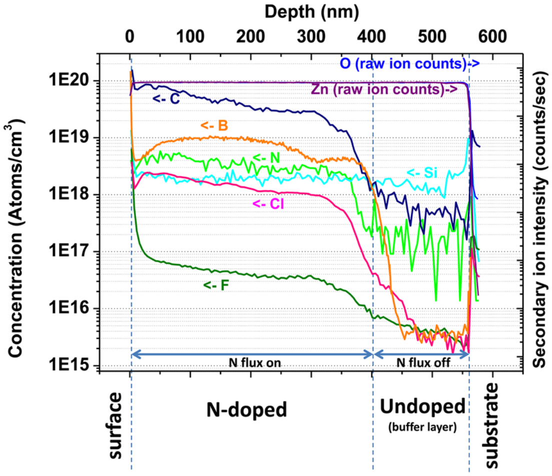

FIG. 2. Profiles of Si, B, N, C, Cl and F as a function of depth into the substrate from the surface. The vertical dashed lines demark the interfaces between different layers.

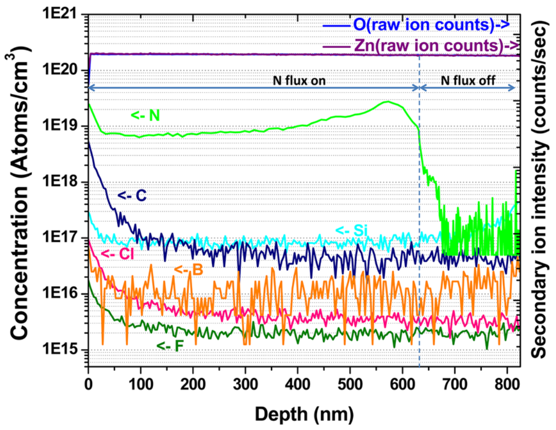

FIG. 3. The N doping depth profile in the ZnO films, grown by using the DT and AP with ZnO passivation layer. The donor-type impurities (Si, B, C, Cl, F) were controlled at a tolerable level.

2×10^{16} cm^{-3}, mobility 10 cm^2/V·s). The specific configuration of the acceptor states introduced by N doping requires further study.

IV. CONCLUSIONS

In a summary, by systematically analyzing the sources of contamination that may be introduced during the epitaxial process of ZnO, we lock the donor-type impurities of Si, B, C, Cl, and F and determine they come from the DT and AP of RF atom sources. After reducing the concentration of these donor-type impurities, the residual carriers concentration of the unintentional doped ZnO film was reduced to 1×10^{15} cm^{-3} and the mobility reached 155 cm^2/V·s. At the same time, the N doped ZnO films exhibited p-type conductivity. The hole concentration was 2×10^{16} cm^{-3}, and the mobility was 10 cm^2/V·s. Our experimental results provide a relatively pure basis for the study of ZnO p-type doping. Further p-type doping studies can focus on constructing shallow acceptor levels and suppressing native point defects (such as V_{O}) self-compensation.

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