Improving SiC Crystal Purity and Electrical Properties with the Use of Getter-Purified Argon Gas

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ABSTRACT

Gaseous nitrogen impurities brought by the carrier gas into the growth chamber can be a major source of contamination during SiC crystal growth. Use of heated getter argon gas purifiers produced by Johnson-Matthey in SiC crystal growth led to a measurable improvement of the purity and electronic properties of the crystals.

BACKGROUND

Conventional semiconductor crystals, such as germanium and silicon, can be manufactured with the levels of background contamination as low as 10^{11} - 10^{12} at/cm³. Although under development for more than 50 years, silicon carbide contains much higher concentrations of background impurities – the purest SiC crystals grown today exhibit impurity concentrations on the order of 10^{13} - 10^{14} at/cm³ for transition metals and about 10^{15} at/cm³ or higher for boron and nitrogen.

From the standpoint of device applications, high frequency semiconductor devices in particular, boron and nitrogen represent the most harmful impurities in silicon carbide. In contrast with many metallic impurities, which have their energy levels deep in the SiC bandgap, boron and nitrogen levels are shallow. This means that at room temperature even small quantities of B and N residing in the SiC crystal lattice would generate enough free carriers to cause significant deterioration of the electronic properties [1].

At the same time, boron and nitrogen are the most stubborn contaminants in silicon carbide, and they are quite difficult to eliminate. Boron can be, typically, traced to graphite used as a material for the construction of growth furniture, while there are several possible sources of nitrogen contamination. Inert gases such as argon or helium are used conventionally as an atmosphere in which SiC crystal growth is carried out. Industrial purity inert gases, even those of "Ultra Pure" grade still contain detectable amounts of nitrogen, typically, on the order of several ppm. This gaseous nitrogen brought by the carrier gas into the growth chamber can be one of the major sources of nitrogen contamination during SiC crystal growth.

The residual nitrogen can be removed from the growth atmosphere and the purity of SiC crystals improved by employing an additional step of gas purification. This additional purification step can be carried out either at the entry-point to each growth station or by purification of the entire gas flow supplied to several growth stations.

GAS PURIFICATION

To examine the benefits of a nitrogen-free carrier gas in SiC growth processes, a Johnson Matthey heated getter argon purifier was introduced into the growth process of a leading US supplier of SiC wafers. The purifier uses zirconium alloys with aluminum (Zr-Al), iron (Zr-Fe), and vanadium (Zr-V-Fe). The getters are typically used in a porous pellet form. The zirconium metals are very reactive with a wide variety of gas species such as O2, H₂O, CO, CO₂, CH₄ and N₂. The chemisorption reactions are irreversible and form oxides, carbides and nitrides via the following reactions:

CO + Zr -> Zr-O + Zr-C CO2 + Zr -> Zr-C + 2 Zr-O N2 + Zr -> 2 Zr-N O2 + Zr -> 2 Zr-N

Zirconium getters are operated at elevated temperatures, typically 400-450C, depending on the gas to be purified and impurities to be removed. The chemical reactions shown above occur on the surface of the metal, and the reaction products then diffuse into the bulk structure, providing clean surface for renewed adsorption and reaction. This reactivation process is carried out continuously at high temperatures.

Getter purifiers are well-suited for SiC growth processes because they are the only technology that can remove nitrogen impurities to parts-per-billion (ppb) levels.

Testing was performed with the PureGuard Wall Mount I heated getter purifier at flows of < 10 slpm. Typical purity performance of the purifier is shown in the table below.



Gas Purity For PureGuard Heated Getter Argon Purifier



Wall Mount III Heated Getter Argon Purifier Maximum Flow: 100 slpm

Use of the Johnson-Matthey gas purifiers in SiC crystal growth led to a measurable improvement of the purity and electronic properties of the crystals. Due to the proprietary nature of the testing conditions, detailed analysis is not available.

[1] T.A. Anderson et al; Mat. Sci. Forum, Vols. 457-460 (2004), p.75.