The ESR Investigation of Brownish Ring at the Surface of Quartz Crucible Used for Cz-Si Crystal Growth

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An ESR spectrum was observed for brownish rings formed at the surface of quartz crucible used in Cz-Si crystal growth. A signal assignable to the E'-center has been detected in the brownish ring. This result is explained by the dissolution of oxygen atoms of vitreous quartz crucible into liquid silicon.

It is well known that the oxygen content of silicon wafers plays a crucial role in device performance and device yield. The oxygen in wafers is incorporated during the growth process of Si single crystal. The main source of oxygen upon crystal growth by the Czchralski method is the quartz crucible used as a charge container. The interface reaction between liquid silicon and the quartz crucible is, therefore, extremely important as far as the oxygen source is concerned.

Brownish rings[1] are often found at the surface of quartz crucible after the Czchralski pulling. Nevertheless, there is little work concerning the mechanism of formation of the brownish rings. Ohta et al.[2] reported that the formation of the brownish rings was due to the foam of silicon monoxide caused by the reaction between molten silicon and vitreous silica of the crucible. This interpretation of silicon monoxide foam suggests that a colored substance is deposited on the surface of quartz crucible .

One will note, however, that the brownish rings surround the crystallized silica, cristobalite, at the surface of quartz crucible. In addition, it is worth noting that the cristobalite is insoluble into liquid silicon.

In the present work, we observed the ESR spectrum of the brownish rings. Many papers have dealt with defect centers in quartz induced by irradiation with γ rays or an optical fiber drawing process.[3-8] The devitrified layers of the sample used for ESR measurements were carefully removed by treatment of dilute hydrofluoric acid. Containing the brownish rings thus treated were packed in a sample tube. An ESR spectrum was measured at the X-band with a JEOL JES-RE2X spectrometer. Microwave power was 1 mW. The *g* value was obtained by referring to the MnO ESR spectrum. The ESR spectrum of the brownish rings measured at room temperature is shown in Figure 1, in which the signals of both sides are due to Mn^{2+} as the *g*-marker, 2.034 and 1.981, respectively. This ESR spectrum is in fair agreement with that of E'-center[7] in γ ray irradiated preform or an optical fiber and the *g* values are listed in Table 1. The best known and most extensively studied intrinsic defect center in quartz is the E'-center, which consists of an electron trapped in a nonbonding sp^3 hybrid orbital on a silicon at the site of an oxygen vacancy. ESR measurements were also carried out at a liquid nitrogen temperature, but no additional signal was detected. It is concluded that the brownish ring contains only E'-center as the defect center.

Table 1. ESR spectrum *g* values

	present work	Irradiated silica preform[7]	Silica fiber[7]
$g_{/\!/}$	2.001^9	2.0019±0.0002	2.0009±0.0002
$g_{\perp}$	2.000^3	2.0006±0.0002	2.0003±0.0002

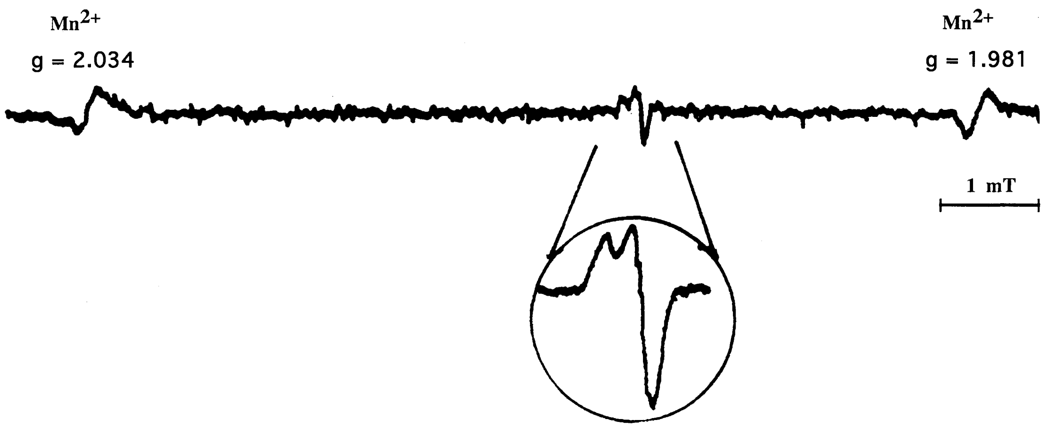

Figure 1. ESR spectrum of the brownish rings measured at room temperature.

This result shows that the appearance of brownish ring is not the deposition of silicon monoxide ($Si + SiO_2 \rightarrow 2SiO\downarrow$) but the deoxygenation of the crucible silica ($\equiv Si-O-Si\equiv \rightarrow \equiv Si\cdot + \cdot Si\equiv + 1/2\ O_2\uparrow$).

Thus, the incorporation of oxygen upon crystal growth by the Czchralski method is explained by the dissolution of oxygen atoms of vitreous quartz crucible into liquid silicon.

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