

Amorphous Silica Containers for Germanium Ultrapurification by Zone Refining

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Abstract—We have studied the wetting behavior of molten germanium on silica ceramics and amorphous silica coatings in vacuum at a pressure of 1 Pa and a temperature of 1273 K. The results demonstrate that the wetting of rough surfaces of ceramic samples and coatings by liquid Ge is significantly poorer than that of the smooth surface of quartz glass. The contact angle of polished glass is $\sim 100^\circ$, and that of the ceramics and coatings increases from 112° to 137° as the total impurity content of the material decreases from 0.120 to 1×10^{-3} wt %. Using experimental contact angle data, we calculated the work of adhesion of molten Ge to the materials studied. Its value for the surface of the ceramics and coatings decreases from 0.45 to 0.20 J/m² with decreasing impurity content, whereas the work of adhesion to a smooth glass surface is 0.55 J/m². We have fabricated fused silica test containers coated with high-purity amorphous silica. Using horizontal zone refining, we obtained germanium samples with a carrier concentration difference on the order of 10^{11} cm⁻³.

Keywords: melt, container materials, amorphous silica, fused silica, ceramic, contact angle, work of adhesion

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INTRODUCTION

The use of germanium single crystals containing as low impurity concentrations and defect densities as possible holds much promise for the development of semiconductor nanotechnologies. They are needed in photovoltaics as substrates for epitaxial III–V optoelectronic structures, which are required for the fabrication of solar cells based on GaInP–GaInAs–Ge systems—high-performance photoconverters offering efficiencies above 39% [1–4].

To fabricate such solar cells, high-purity, dislocation-free crystals are necessary, because dislocations and unintentional impurities lead to lattice mismatch between Ge and III–V compounds, making it difficult to grow high-quality epitaxial layers on germanium substrates [4, 5].

Dislocation-free high-purity germanium helps to resolve issues pertaining to the use of silicon in the fabrication of radiation-resistant power MOSFET transistors, which are employed in power supply units, voltage converters, drive control units and other electronic devices in space equipment. The high carrier

mobility in dislocation-free germanium, up to ~ 3000 cm²/(V s), which is twice that in Si, allows it to be used with great success in the fabrication of space-grade high-speed digital devices [6].

Extrapure-grade germanium is used to fabricate radiation-resistant gamma-ray detectors, which require crystals with a concentration of electrically active impurities in the range from 10^9 to 10^{11} cm⁻³ [4, 5]. In the technology of the preparation of extrapure germanium and low-dislocation germanium crystals, the melt container material plays an important part. A standard material for this purpose is ultrapure-grade graphite. However, when graphite melt containers are used, the germanium melt becomes contaminated with B, Ga, and P. At low concentrations of these impurities, their effective distribution coefficients approach unity and, accordingly, they cannot be removed [7]. One way to resolve this issue is to employ new container materials. These include boron nitride, silica-based materials, sapphire, glassy carbon, and aluminum nitride. According to a large

amount of data, amorphous SiO₂ in the form of fused silica or ceramics is the best choice [4, 5, 8, 9].

During germanium purification by crystallization, impurities present in the container material may enter the melt and contaminate it, so the wettability of the container by the melt is an important factor, because it determines the dissolution kinetics of the container material. Moreover, the contact angle influences the shape of the melt meniscus and, accordingly, the adhesion of the coating material to germanium, which in turn influences its ability to separate from the container in the unloading step [9]. Available data on the wettability of SiO₂-based materials by molten germanium are limited to results for polished surfaces of fused silica [10, 11].

The purpose of this work was to study the wetting properties of molten germanium on rough surfaces of silica ceramics differing in purity and on amorphous silica coatings on the surface of fused silica. We produced test silica containers with high-purity silica coatings and used them in germanium purification by zone refining.

EXPERIMENTAL

Ceramic articles were produced by slip casting. To this end, we prepared an aqueous slip containing 70 wt % amorphous SiO₂ powder, which was sintered at a temperature of 1450 K for 2 h [12].

Silica powders ranging in total impurity content from 0.120 to 0.020 wt % were prepared by grinding quartz glass in a planetary mill using agate vials, followed by purification in a 3 : 1 mixture of the HF and HNO₃ acids. High-purity amorphous SiO₂ containing 0.010 to 0.001 wt % impurities was prepared by a sol-gel process using extrapure-grade silicon tetrachloride (SiCl₄) [13].

The synthetic SiO₂ powders were used to prepare ceramics and produce ceramic coatings up to 100 μm thick on quartz glass substrates by slip casting [12]. In addition, ~20-μm-thick SiO₂ coatings were produced on fused silica by repeatedly wetting its surface with silicon tetrachloride, followed by hydrolysis in humid air, drying, and annealing at a temperature of 1253 K [14].

The contact angle of molten germanium on SiO₂-based ceramics and coatings was determined on a Kaplya apparatus (State Research and Design Institute for the Rare-Metals Industry) using substrates in the form of rectangular plates 2 × 2 cm² in area. The measurements were performed in vacuum at a residual pressure of 1 Pa and a temperature of 1273 K. The reference sample used in our wetting experiments was a polished fused silica plate.

Impurity concentrations in our samples were determined by atomic absorption on a Solaar M spectrometer (Thermo Electron Corp.). To examine the microstructure of the samples and assess their surface roughness (surface height distribution), we used an Axio Observer A1 optical microscope.

Germanium was zone-refined using a Kristall-808 unit (Freal and Co.) and test containers with a high-purity silica coating on their working surface. As a feed stock, we used GPZ zone-refined germanium with a resistivity of at least 47 Ω cm. The process was run in a hydrogen atmosphere. The molten zone length was 5 cm.

The room-temperature resistivity of GPZ polycrystalline ingots was measured by the two-probe method. The resistivity of the zone-refined germanium was also measured by the two-probe method at room temperature, using monocrystalline blocks cut from the ingots. In addition, we performed resistivity measurements at 213 K by a microwave method. The microwave measurements were performed with an Angara 2 system. The carrier concentration difference was determined by capacitance–voltage (*C–V*) measurements with a QuadTech QT7600B LCR meter.

RESULTS AND DISCUSSION

In our experiments concerned with the wetting behavior of molten germanium, we used ceramic samples prepared under identical conditions from amorphous silica powders with identical particle size compositions, similar in physical properties and microstructure (Fig. 1).

The grain size in the ceramics ranged from 1 to 20 μm. The surface roughness value was 5–10 μm, the density of the ceramics was 1.95 g/cm³, and their porosity was ~12.0%. The ceramic samples differed in impurity content, which ranged from 0.001 to 0.120 wt %. In all of the samples, the dominant impurities were Na, K, Al, and Fe. The reference sample (polished quartz glass) had a similar range of impurities, and their content was 0.050 wt %.

Figure 2 is a photograph of a molten germanium drop on the surface of a ceramic sample containing 0.01 wt % impurities. At this impurity content, the contact angle is 133°.

The contact angle of molten germanium on the surface of polished quartz glass was determined to be ~100°, which is comparable to the corresponding equilibrium contact angle reported by Cröll et al. [10] and Kaiser et al. [11]. Figure 3 demonstrates that the contact angle of the ceramic samples increases from 112° to 137° as the total impurity content decreases from ~0.120 to 0.001 wt %.

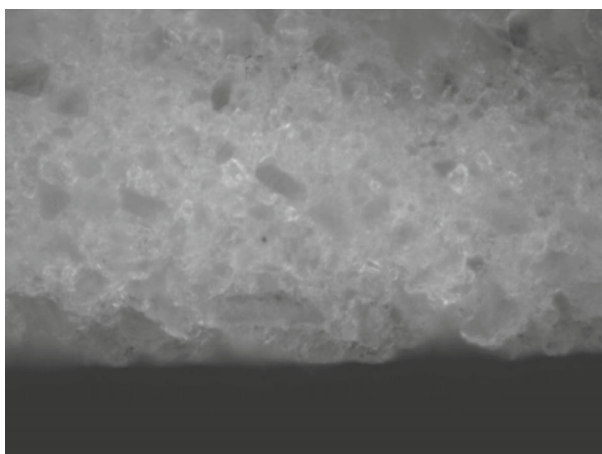


Fig. 1. Typical microstructure of the ceramic samples, 700 \times .

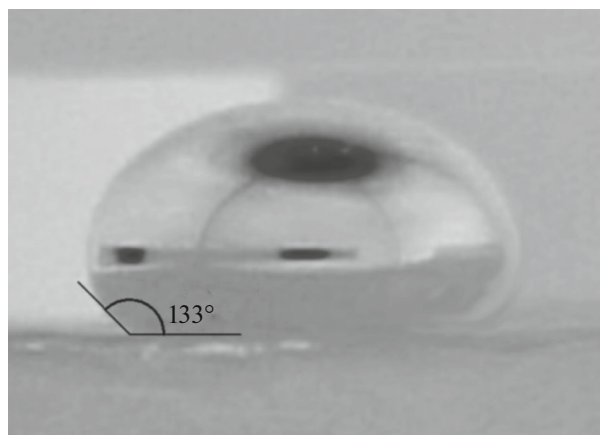


Fig. 2. Photograph of a molten germanium drop on the surface of a ceramic sample containing 0.01 wt % impurities.

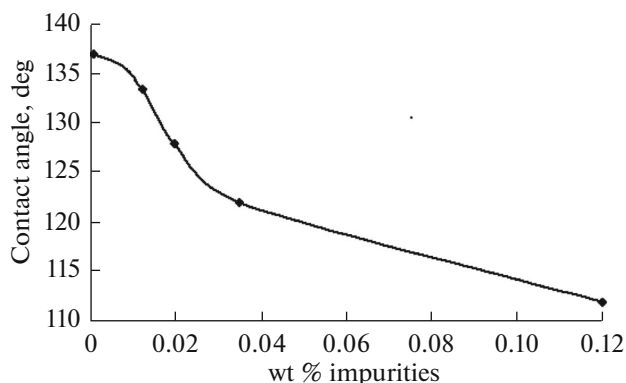


Fig. 3. Contact angle as a function of the percentage of impurities in the ceramic samples.

Our measurements demonstrate that, at a given impurity content, the surface roughness, wetting behavior, and quantitative wetting characteristics of $\sim 20\text{-}\mu\text{m}$ -thick high-purity amorphous SiO_2 coatings on fused silica (Fig. 4) are identical to those of the ceramic material.

The results obtained in this study lead us to conclude that the wetting of rough surfaces of ceramic samples and amorphous SiO_2 coatings by molten germanium is significantly poorer than that of the smooth surface of quartz glass. This distinction can be accounted for in terms of the Wenzel equation:

$$\cos \theta_r = K \cos \theta_0, \quad (1)$$

where θ_r is the contact angle of a melt on a rough surface, θ_0 is the true contact angle (contact angle on a smooth surface), and K is a roughness coefficient ($K > 1$).

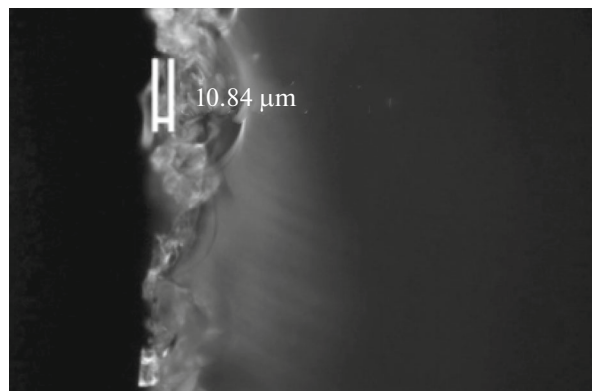


Fig. 4. High-purity silica coating on the surface of fused silica.

This equation is consistent with the experimentally observed increase in contact angle with increasing surface roughness in the case of a nonwetable surface.

Substituting the measured contact angle into the Young–Dupre equation,

$$W = \sigma(1 + \cos \theta), \quad (2)$$

where σ is the surface tension coefficient of molten germanium and θ is the contact angle, we calculated the work of adhesion W of molten germanium to the

Table 1. Impurity composition of the coating material, 10^{-4} wt %

Al	Cu	Ni	Cd	Cr	Fe	Mn	Pb	Na
≤ 3	≤ 0.3	≤ 0.3	≤ 0.02	≤ 0.5	≤ 3.0	≤ 0.1	≤ 0.04	≤ 1.0



Fig. 5. Test containers with germanium charges.

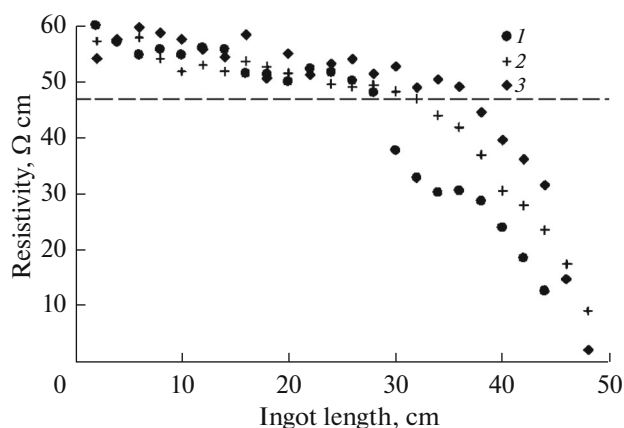


Fig. 6. Resistivity profiles along germanium samples zone-refined by (1) 5, (2) 10, and (3) 15 molten zone passes.

Table 2. Resistivity of zone-refined germanium at 213 K

Number of zone passes	5	10	15
Resistivity, Ω cm	936	4100	6000

Table 3. Carrier concentration difference at a temperature of 77 K

Number of zone passes	5	10	15
Carrier concentration difference, cm^{-3}	4.5×10^{12}	5.2×10^{11}	1.2×10^{11}

materials under investigation. The surface tension coefficient of molten germanium was found as [10, 11]

$$\sigma = 591 - 0.08(T - T_m)10^{-3} \text{ N/m}, \quad (3)$$

where T is the measurement temperature.

The calculation results indicate that, as the total impurity content decreases from 0.120 to 0.001 wt %, the work of adhesion of molten Ge to the surface of the amorphous SiO_2 ceramics and coatings decreases from 0.45 to 0.20 J/m^2 , whereas that for a smooth glass surface is 0.55 J/m^2 .

We fabricated fused silica test containers in the form of 500-mm-long, 50-mm-wide boats coated with an $\sim 20\text{-}\mu\text{m}$ -thick synthetic silica layer as described by Averichkin et al. [14]. The total impurity content of the silica layer was ~ 0.001 wt %. Table 1 indicates the impurity composition of the coating material, and Fig. 5 shows the containers with germanium charges.

Using the test containers, we purified germanium by zone melting. The zone refining process consisted of 5, 10, or 15 molten zone passes. Figure 6 shows resistivity profiles along the zone-refined germanium samples.

These data demonstrate that, after zone refining, the fraction of the ingot with $\rho \geq 47 \Omega \text{ cm}$ is approximately 50%. The resistivity values above 47 $\Omega \text{ cm}$ at the beginning of the ingot are due to the fact that, after zone refining, the measurements were performed on monocrystalline blocks cut from the solidified ingot, as distinct from the resistivity measurements on GPZ polycrystalline samples, whose results are influenced by the presence of surface states, as shown previously [15].

The resistivity of the zone-refined germanium at a reduced temperature on the order of 213 K was found to vary from 936 to 6000 $\Omega \text{ cm}$, depending on the number of molten zone passes, as demonstrated in Table 2.

Table 3 presents the carrier concentration difference data for germanium crystals after zone refining. The testing results for the zone-refined germanium ingots demonstrate that, after 15 zone passes, the carrier concentration difference in the ingots is $1.2 \times 10^{11} \text{ cm}^{-3}$. Using deep level transient spectroscopy [16], the concentration of deep levels in the upper half of the band gap was determined to be $\sim 10^{10} \text{ cm}^{-3}$.

CONCLUSIONS

In the preparation of extrapure-grade germanium, it is reasonable to use amorphous silica melt containers produced either by ceramic processing route or from fused silica coated with high-purity SiO_2 .

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