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Investigation of Al-ZERODUR interface by Raman and secondary ion mass-spectroscopy

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Abstract. The interface of ZERODUR ceramics and thin aluminium film was investigated by Raman and secondary ion mass-spectroscopy techniques. Possible chemical reactions at the interface is briefly analyzed and compared with experimental data. Contributions of amorphous and crystalline phases of ZERODUR to Raman spectra are discussed.

Keywords: ZERODUR ceramics, Raman spectra, secondary ion mass-spectroscopy.

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1. Introduction

ZERODUR is glass ceramic widely used in different brunches of industry and science. For example, it has decisive advantages for application in modern LCD lithography. Among the most important advantages of this material are its zero thermal expansion, good processability and very low surface roughness. From the chemical viewpoint, ZERODUR consists of oxides Li_2O–SiO_2–Al_2O_3. It is synthesized at temperatures 700–1000°C. In order to stimulate formation of the nucleation center, titanium oxide is added to the starting charge. This ceramics has both crystalline and amorphous phases. The crystalline phase is represented by crystallites of nanometer sizes (d = 50–70 nm). The crystalline phase has a negative linear thermal expansion, while that of the amorphous phase is positive. This results in zero thermal expansion coefficient in a rather wide temperature range.

ZERODUR serves as the mirror substrate material for large-scale telescopes. Currently the world's largest and most powerful telescope, has four main mirrors made of ZERODUR glass ceramic, each with the surface of over 50 square meters and the diameter of 8.2 meters. Very large mirrors and other systems may be composed of many components made of ZERODUR. So, assembling these components is an important engineering task. Different components made of ZERODUR can be jointed together by diffusion welding by using the aluminium film of 100 nm thickness previously deposited on the surface in a vacuum chamber. The performance of such welding depends critically on chemical and physical processes at the aluminium-ZERODUR ceramics interface. The aim of this work is to investigate these processes at the interface of ZERODUR ceramics with aluminium.

2. Experimental results and discussion

Raman spectroscopy is known to be an excellent tool to study local order and its perturbation in both crystalline and amorphous materials. Because of the short-range order is preserved in amorphous material, Raman spectra are expected to be similar for amorphous and crystalline phases of investigated material. However, Raman spectroscopy does not allow to decide whether bond angle or bond length fluctuations are predominant. In the present investigation Raman scattering has been measured on selected samples of ZERODUR ceramics. The Ar laser (λ = 514.5 nm, $P \approx$ 100 W) was used to excite Raman spectra. Experimental spectra were recorded in the photon counting mode.

As the microstructure of investigated material composed from crystalline and amorphous phases is unknown, modeling the amorphous network is difficult. However, it is clear that interpretation of a measured Raman spectrum of one of these phases is possible if there is information on the vibration spectrum of another phase. Taking this into account, the vibration spectrum of SiO_2 film grown on a sapphire substrate was measured first of all. The necessity of such measurements is explained by the fact that the characteristic spectral lines corresponding to chemical bonds of SiO_2 should be observed also in ZERODUR. The SiO_2 glassy represents the amorphous network from silicon atoms tetrahedrally surrounded by oxygen atoms. The tetrahedrons are bound with each other by means of oxygen atoms, so Si-O-Si bridges with the angle

between bonds close to 150° is formed. In other words, in the amorphous network each of Si atom is surrounded by four oxygen atoms and, in turn, each atom of oxygen is surrounded by two atoms of Si [1].

In Fig. 1, the vibration peaks with frequencies about 800 and 100 cm^{-1} are shown. The peak at the frequency 400 cm^{-1} can be attributed to Si-O rocking vibration of SiO_2 tetrahedron, and the peak at 800 cm^{-1} is connected to vibration of chemical bond bending of Si-O-Si bridge [2]. The intensive narrow peak at 378 cm^{-1} is caused by radiation of plasma in gas-discharge tube of Ar laser.

Curve 2 in Fig. 1 represents the Raman spectrum of the same film after thermal annealing in nitrogen atmosphere for 15 minutes at the temperature 500 °C. It is seen that weak peak occurs also in the range of frequencies around 490 cm^{-1}. It can be attributed to Si-Si bond. It has been shown in [3] that thermal annealing of SiO_2 films results in the composition transformation

$$2\ SiO_x \rightarrow x\ SiO_2 + (2 - x)\ Si. \qquad (1)$$

For example, in those parts of SiO_2 film where the stoichiometry is breaked, elementary silicon can arise at high temperatures. As shown in [4], high temperature annealing of SiO_2 non-stoichiometric films results in broad-band peak with maximum centered at 490 cm^{-1}, which may be attributed to Si-Si bond. This means that clusters of amorphous silicon are formed.

To obtain information about vibrations in Al_2O_3, the overall (depolarized) Raman spectrum of sapphire was measured, Fig. 2. As seen, three peaks at 419, 646, and 751 cm^{-1} are clearly observed in the spectrum. Peak at 378 cm^{-1} is also observed as well as in the spectrum of SiO_2. Since the scattering properties of sapphire is less than the film of SiO_2, this band in Fig. 2 has a lower intensity. In the case of amorphous Al_2O_3 films, it is possible to suppose that the measured spectrum should correspond qualitatively to that shown in Fig. 2, but the width of the observed peaks may be more considerable.

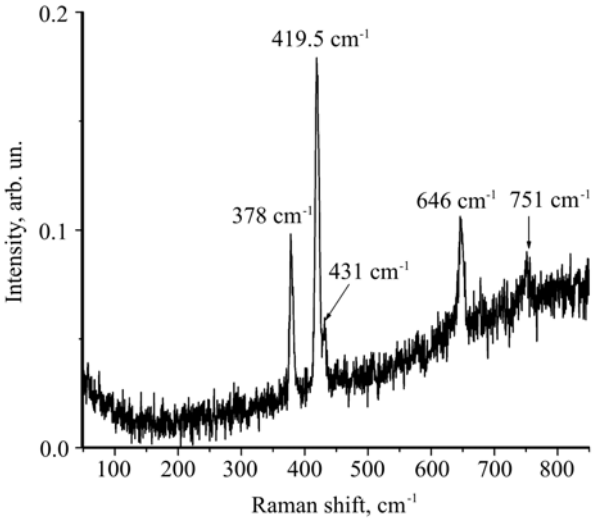

Fig. 2. Raman spectra of sapphire (α-Al_2O_3).

In order to measure Raman spectra in ZERODUR ceramic samples, the latter were specially prepared. For this purpose, samples were cut in the shape of parallelepiped 15×15×40 mm. Their lateral faces were polished. One of the face was covered by thin film of Al thermally evaporated in a vacuum system. After that samples were annealed at temperature 400 °C within 15 minutes. The metallic layer was then removed in such a manner that the trace of Al was saved in one-half of a sample. The geometry of measurements is shown in Fig. 3.

Fig. 4 shows the Raman spectra measured in several parts of the ZERODUR sample, which are indicated in Fig. 3. The spectra 1 and 2 were recorded using the standard 90° technique. In the spectrum obtained at bulk excitation of a sample, two broad peaks are observed in two spectral ranges 400 – 500 and 100 – 200 cm^{-1}. The edge of the first peak at frequencies less than 50 cm^{-1}

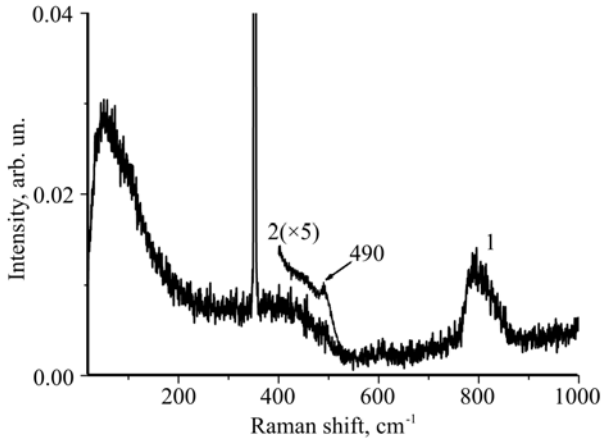

Fig. 1. Raman spectra of the SiO_2 amorphous film (curve 1) and the same film annealed at T = 500 °C for 15 min (curve 2).

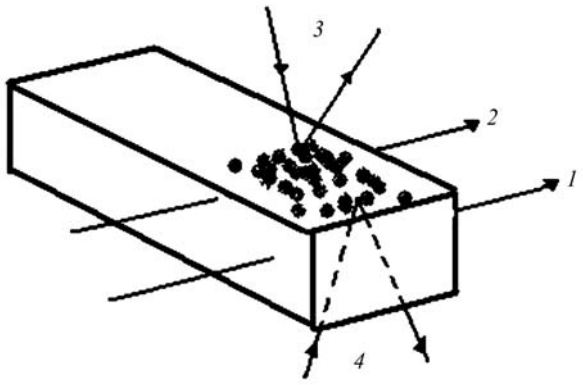

Fig. 3. The geometry of the experiment: 1-4 different positions for Raman spectra detection.

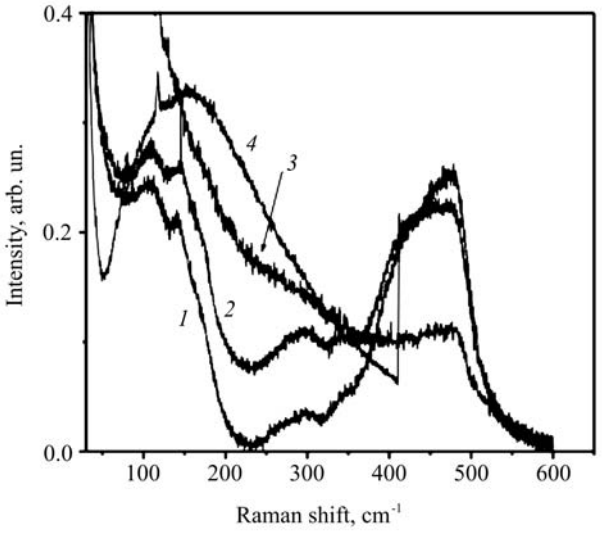

Fig. 4. Raman spectra of ZERODUR: curves 1-4 correspond to positions indicated in Fig. 3.

represents the wing of the Rayleigh line. From the comparison of this spectrum with Raman spectra of SiO_2 and Al_2O_3 (Figs 1 and 2) one can suppose that the peak in the spectral range 100 – 200 cm^{-1} can be attributed to SiO_2, whereas that peak in the spectral range 400–500 cm^{-1} is attributed to Al_2O_3. In the crystals of corundum γ-Al_2O_3 or sapphire-Al_2O_3, any aluminium atom occupies position with octahedral surrounding of oxygen atoms. In amorphous phase, it has the same nearest surrounding. However, in the amorphous network little changes of angles and lengths of chemical bonds can occur. This results in changes of vibrations frequencies inherent to the elementary octahedron, and this is a cause of a large broadening of observed spectral peaks.

It is well known that reactivity of Al is higher as compared to Si. Thus, it may be reasonably assumed that the diffusion of Al into ZERODUR is accompanied by the chemical reaction

$$4\ Al + 3\ SiO_2 = 2\ Al_2O_3 + 3\ Si. \qquad (2)$$

This transformation is possible, if the heat of reaction (2) is negative. Note that the energy of chemical bonds in Al_2O_3 is approximately 20 % higher than in SiO_2. This can be regarded as additional proof that exchange reaction can be carried out at 400 °C. However, there arises a problem concerning possible positions of Al in the investigated ceramics. In the crystal lattice of SiO_2, aluminium can occupy both substitutional and interstitial positions. Because of Al has smaller radius as compared to Si, substitution of Si by Al in SiO_2 tetrahedral structures will cause a shift of peak frequencies towards higher frequencies. Curve 4 in Fig. 4 represents the Raman spectrum measured at the part of the surface where this process is the most probable. This result qualitatively confirms the above reasons. On the other hand, Al can substitute Si in amorphous phase, too. In this case, it is possible to expect that clusters of amorphous Si are formed. The Raman spectrum shown in Fig. 4 (curve 3) was measured from the surface that has been previously covered by Al. The weak peak at 490 cm^{-1} can be attributed to Si-Si bonds. Furthermore, the behavior of experimental curve in the spectral range 400-500 cm^{-1} qualitatively coincides with curve 2 in Fig. 1, which corresponds to silicon amorphous clusters in SiO_2.

In addition, it is necessary to note that the existence of the alumina Al_2O_3 amorphous phase should not be excluded in glass ZERODUR. The structure of the amorphous network is unknown in this case. If chemical bonds in the amorphous phase are occupied, it is possible to suppose that in this case the structural unit should be AlO_3. In this case, each atom of Al is bound with three atoms of oxygen, and each atom of oxygen is bound with two atoms of aluminium through a bridge Al-O-Al. Investigation of Raman spectra in $Pr_xNd_{1-x}AlO_3$ crystals [5] that contain the AlO_3 as structural units showed that AlO_3 has vibration frequencies in the spectral ranges 50, 150, 270, and 480 cm^{-1}. These frequencies are in good agreement with measured spectra (curve 1 and 2, Fig. 4).

Mechanical properties of joint may depend on chemical processes at the metal-ZERODUR interface which are carried out during their manufacture and storage. Chemical reactions may include interdiffusion of metal and components of ZERODUR, formation of mixture phases and new chemical compounds. Besides, the possible out-diffusion of components (Si, Li) into the metal can modify its physical properties. Naturally, the diffusion processes at the interface depend on temperature. In this case, temperature is an important parameter not only from the view point of diffusion velocity but the activation energy of possible chemical reactions, too. For example, the exchange reaction (2) seems to be the most simple type of possible chemical reactions at the interface.

In order to clarify physical properties of the Al-ZERODUR interface, the secondary ion mass-spectroscopy (SIMS) measurements has been carried out. The SIMS profile measurements were taken with IMS-4F ("Cameca"). SIMS profiling was performed with a 4 keV Ar^+ primary beam scanned over a crater approximately 2×2 mm. The results of SIMS measurement are shown in Fig. 5. The out-diffusion of Si into the metal film is clearly seen. Moreover, the increase of Si content at the surface of the metal film (the so-called floating of Si) is observed as well. This result is in accordance with those of Raman scattering measurements described above.

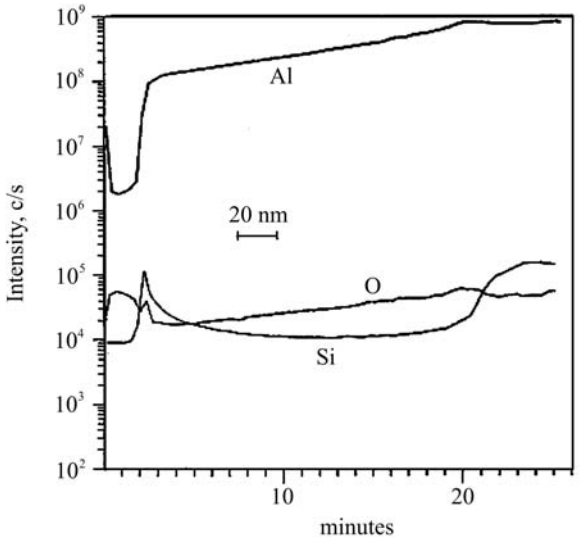

Fig. 5. SIMS profiles of ZERODUR measured from the surface covered by aluminium layer.

3. Conclusions

1. Raman spectra are investigated in ZERODUR ceramics at room temperature. Experimental data are analyzed taking into account contributions of amorphous and crystalline phases of ZERODUR to measured spectra.

2. Possible chemical reactions and interdiffusion at the interface of aluminium and ZERODUR ceramics are studied.

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