

Industrial Revolution by New Electrically Conductive Oxide Glass: *NTA Glass*TM

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New electrically conducting oxide glass was discovered by Nishida¹⁾ in 2001. Electrical resistivity (ρ) of this glass can be changed from several mega- to several Ωcm ,¹⁻³⁾ and is now being utilized in several industrial fields. This glass has attracted much interest, since it might bring about innovation or industrial revolution.²⁾ It was registered as *NTA glass*TM (nano- technology or new technology assorted glass) by Tokai Industry Corporation in 2006.

Silicate (SiO_2 -based) glass has been used for more than 4500 years since the first fabrication of glass ware in the ancient Mesopotamia. Silicate glass is now generally used in our life as glass ware, glass bottle, window glass, *etc.* It is also utilized in the industrial field because of its easy cutting, mechanical grinding or machining and also for microfabrication of micrometer size. For the processing to the level of “nanometer” size, *i.e.*, hyperfine processing or nanoprocessing, FIB (focused-ion beam) is generally used with charged particles like Ga^+ . Silicate glass with high ρ , however, is no good for the nanoprocessing since the positive charge accumulated on the surface of the insulating glass results in a bending of the beam line of positively charged particles, lowering the precision of the nanoprocessing. A large amount of positive charge will accompany an electrostatic destruction or cleavage. This problem could be solved by the development of new electrically conductive oxide glass that can immediately neutralize the positive charge.

Some industrial applications of *NTA glass*TM have already been initiated in Japan. *NTA glass*TM is a kind of vanadate (V_2O_5 -based) glass of which electrical conductivity or resistivity can easily be regulated by changing its chemical composition, and also by changing the temperature and time of annealing: additional heat treatment after melting.³⁻⁵⁾ Photograph dedicates 5 patterns with linewidth of 100 nm, 200 nm depth and 3 μm length. It is noted that nanoprocessing of *NTA glass*TM ($\rho = 137 \Omega\text{cm}$) was completed after 1-min FIB procession with Ga^+ ions (40 kV and 70 pA). Precision of the photograph can be seen from the small photograph; surface of the unpolished *NTA glass*TM had asperity of 5 ~ 50 nm.

Structure of silicate glass is composed of 3D-network in which each Si^{IV} atom is coordinated to 4 oxygen atoms, forming distorted SiO_4 tetrahedra. Each oxygen atom occupying the corner of SiO_4 tetrahedron is shared by two Si^{IV} atoms to form Si-O-Si bond. It is noted that silica or silicate glass is an insulator since there is no extra valence electrons in the outermost orbital (3s and 3p orbitals) that can contribute to the electrical conduction.

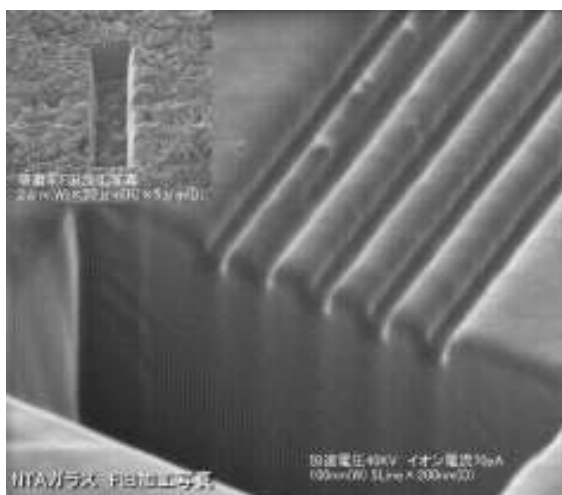


Fig. 1. *NTA glass*TM fabricated with FIB (Ga^+)

In the case of vanadate glass, by contrast, V^{IV} has one valence electron in the outermost orbital (3d orbital), causing a step-by-step electron (small polaron) hopping from V^{IV} to V^V . It is well known that V_2O_5 has a layer structure composed of VO_5 pyramids. Nishida *et al.* elucidated that alkali vanadate glass, like sodium or potassium vanadate glass has a pseudo-chain structure.^{4,5)} They also discovered that barium vanadate glass has a 3D- network structure composed of VO_4 and VO_5 units.¹⁻³⁾ It is considered that vanadate glass generally has lower chemical durability than silicate glass, because V=O bond of VO_5 unit is not used for the V-O-V bond formation, and is chemically reactive.

Chemical bond strength of *NTA glass*TM is widely distributed; 3.9~4.9 and 2.6 eV for V-O and Fe-O bonds, respectively,²⁾ and 1.4 eV for Ba-O bond that plays a role of network modifier: NWM.²⁾ A variety of chemical bond strength will be associated with the easy mechanical and optical processing by using diamond cutter, FIB, laser, *etc.*

In the case of FIB nano- or microprocessing procedure, positive charge of the particles (*e.g.*, Ga^+) must be neutralized by electrons, like 3d-electrons on the V^{IV} atoms constituting 3D-network, lest the precision of nanoprocessing should be lowered. High electrical conductivity or low resistivity is a requisite for the successful nanoprocessing of *NTA glass*TM. For example, *NTA glass*TM with ρ of 10 Ωcm is estimated to enable the nanofabrication with a current of 10 nA and a voltage of 40 kV.²⁾ Under this condition, it is expected that several hundreds patterns will be fabricated in 1 h. These experimental results prove that *NTA glass*TM is a desirable material for the fabrication of “millimeter” to “nanometer” size.

Temperature of *NTA glass*TM with ρ of several ten Ωcm could be increased to higher than 50 °C by applying several ten V of voltage. *NTA glass*TM will be utilized as a cooling unit like Peltier device. Electrical resistivity of semiconducting *NTA glass*TM is decreased at higher temperature, *e.g.*, it decreased from 23 to 11 Ωcm when the temperature was increased from 25 to 100 °C. Electrical conductivity or resistivity of *NTA glass*TM can easily be regulated by changing the annealing condition of temperature and time for the structural relaxation of the glass network, as described above. This is the most important and outstanding feature of *NTA glass*TM, as confirmed by Mössbauer spectroscopy.³⁻⁵⁾

*NTA glass*TM is now commercially used as an electron-emitting probe for “ionizer”. Application of *NTA glass*TM to the electric bulb working under the voltage of several V will bring about low cost performance or energy saving, if the distance between two electrodes were fabricated to several nanometers. It is expected that *NTA glass*TM would be utilized for the incubation box of bacteria, DNA chip, electrophoresis, MEMS, *etc.* for attaining real innovation or industrial revolution.

References

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