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The energy band structure of anodic porous alumina

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Background

Metal/Metal-Oxide/Metal (MOM) structure exhibits a drastic resistance change when applying external voltage. These systems have attracted much attention for the application in the next generation memory device, such as resistive random access memory (ReRAM). Especially, anodic porous alumina (APA) is a key material for fabrication of nano-devices. APA films are well-known in self-organized nano-structure. Each unit cell with a nano-hole in the center forms a honeycomb structure. One can fabricate the large area of well-ordered nano-structure by controlling anodization parameters. Bistable resistive switching and memory effect have been reported for this system [1]. Since a design guide for APA-ReRAM based on a switching mechanism has not been clarified, its development is less advanced than other candidates for next-generation nonvolatile memories. Therefore, elucidation of a switching mechanism is currently a very important issue in the development of APA-ReRAM.

Abstract

From the Nuclear Magnetic Resonance (NMR) and Electron Energy Loss Spectrum (EELS) spectrum [2,3], APA film has high-density oxygen vacancies in the nano-walls. These results suggested that the confined nano-wall structure and the oxygen vacancies in the nano-walls were the origin of the switching mechanism of this system. However, direct evidence has not yet been observed, i.e. oxygen vacancy level and the different band structure between On state and Off state. Then, we measured EELS and Ultraviolet Photoemission Spectroscopy (UPS) to confirm the electronic structure of this sample. In this experiment, we try to clear the band structure near the Fermi levels (E_F) corresponded to the conduction of these system.

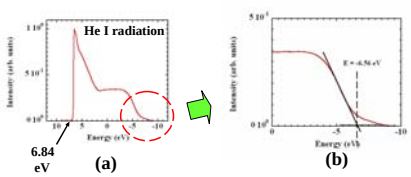
Experiment

1.UPS Ulvac-Phi ESCA-5800 (UV-150H)
He I (21.22 eV) 8W, ϕ 800 nm

2. EELS JEOL JEM-2100F + Gatan 836 GIF Triden
200 kV

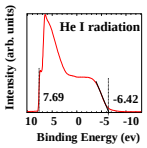
3. Sample preparation
APA (2step method) [4].

UPS measurements



Ionized potential energy = 21.2 – (6.84+6.56)
= 7.8 eV

Fig. UPS results of the APA valence band excited by He I line. (b) is the enlargement of the spectra near the 6.0 eV.



Ionized potential energy (eV)
= 21.2 – (7.69+6.42)
= 7.11 eV

Fig. UPS results of the sapphire single crystal valence band exited by same He I line.

The valence band structure of the APA is similar to the sapphire's one.

EELS measurements

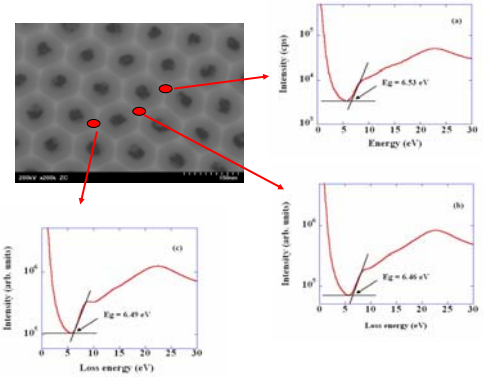
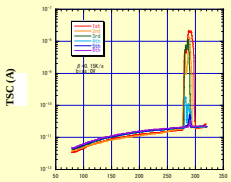


Fig. Electron energy loss spectrum of the APA at beam energy 200 eV.

All points of E_g were estimated to be about 6.5 eV.
These values are smaller than those of the sapphire's one.
(Sapphire's E_g was 8.0 eV)

Thermally Stimulated Current (TSC) of APA-ReRAM

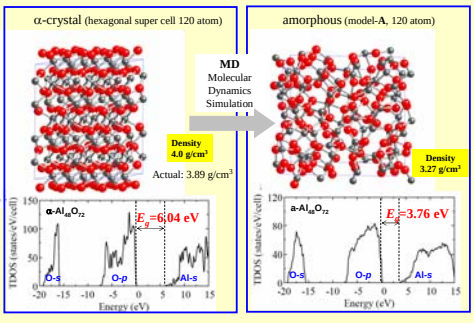


Activation energy of trap electron
$E_t = kT_m \ln(T_m^4/\beta)$
k : Boltzmann constant
T_m: Peak temperature
β : Rate of temperature rise

E_t = 0.58~0.62eV (low-level from the bottom of the conduction band)

Localized electron state in narrow energy levels

Computer simulation by the first principle and molecular dynamics method



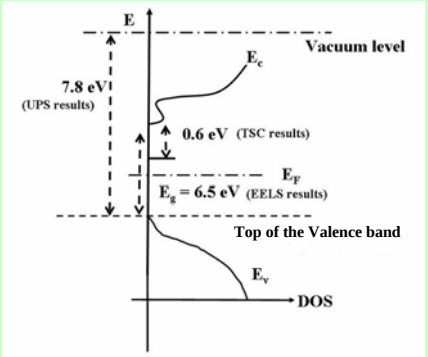
These experimental results were compatible to the first-principle simulation results reported by Momida et al.

	Band gap Eg (eV)	
	sapphire	amorhous alumina
Simulation	6.04	3.76
Experimental	8.00	6.50

Calculated energy gap values of sapphire and amorphous alumina are smaller than experimental band gaps. The degree of band gap reduction is from 2.28 to 2.50 eV.

There is an experimental fact that an approximate linear relationship exists between band gap and average coordination number of Al sites of Al_2O_3 [6]. Therefore, reduced band gaps of the amorphous alumina also seems to be due to their Al and O atomic sites having a lower coordination number.

Band structure of APA



Conclusion

In summary, the electronic structure of the APA were investigated. We have been estimated to be the electronic structure of the APA. From the UPS measurement, the porous valence band consists of an ionic gap of 7.8 eV. From the EELS measurement, the band gap of APA was estimated to be about 6.5 eV. Ionic gap of APA was similar to the sapphire, on the other hand, band gap value of APA was smaller than that of sapphire's. From the calculation study and experimental fact, reduced band gap of APA also seems to be due to their Al and O atomic sites having a lower coordination number.

Acknowledgement

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References

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