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Vibrational Analysis of Evaporated Si and SiO Film by Inelastic Electron Tunneling Spectroscopy

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Inelastic electron tunneling spectroscopy has been used for obtaining the vibrational spectra of the thin films of evaporated Si and SiO. The analysis of the tunneling spectra shows the formation of SiH species. These hydrides are formed from the reaction with residual water molecules in the vacuum system during the evaporation.

There is considerable interest in investigations of metal thin films. Inelastic electron tunneling spectroscopy (IETS) is a technique for measuring the vibrational spectrum of the thin film insulator of a metal/insulator/metal tunneling junction at cryogenic temperatures. Analysis of the spectra gives information on the surfaces and interfaces of the thin film insulators. The properties and reactivities of alumina and magnesia have been intensively investigated by IETS.[1] Tunneling spectra of SiO were obtained from $Pb/SiO/Al_2O_3/Al$ junctions prepared by evaporating SiO on the alumina surfaces.[2-4] The spectra of SiO_2 in similar junctions[5] and those of oxidized Si wafers[6,7] have also been reported. The tunneling spectrum of Si has previously been measured;[5] however, detailed analysis of the spectrum and comparison with other vibrational spectra of Si films were not made. In this paper, we report the tunneling spectra of $Pb/Si/Al_2O_3/Al$ junctions. The spectra of SiO have also been measured. The analysis of these spectra and the comparison with the infrared and Raman spectra of Si and SiO films provide the information on the nature of thin films of Si and SiO.

The junctions were prepared in a vacuum evaporator evacuated with a liquid nitrogen-trapped 4-inch diffusion pump. The details have been described before.[8] Aluminium (99.999%) was evaporated from a molybdenum boat to form strips at a pressure of 10^{-6} Torr (1 Torr = 133.322 Pa). Their surfaces were oxidized in an oxygen-dc glow discharge. Silicon (Wako Chemicals, 99.9999999%, 300 Ω cm) or silicon monoxide (Rare Metallic Co., 99.99%) was evaporated on the alumina surfaces for 2 - 3 s with an evaporation rate of 1.2 nm/s. The surfaces of the deposited Si and SiO films were observed with a scanning electron microscope and a transmission electron microscope and were found to be smooth. The junctions (1 mm^2) were completed with an evaporated Pb (99.999%) strip. The tunneling spectrum was obtained with a bridge circuit and a lock-in amplifier (NF LI-574A) at a liquid-helium temperature (4.2 K).[8] The peak positions of the spectrum were corrected by -1 meV (-8 cm^{-1}) owing to the energy gap of the superconducting Pb electrode.[1] The accuracy of the peak position was estimated to be ± 1 meV (± 8 cm^{-1}) because of the large peak width of the tunneling spectrum of Si and SiO.

The tunneling spectra of the $Pb/Si/Al_2O_3/Al$ and $Pb/SiO/Al_2O_3/Al$ junction are shown in Fig. 1. The spectrum of the $Pb/Al_2O_3/Al$ junction is also shown for comparison. The thickness of the evaporated Si and SiO films was calculated to be 3.0 ± 0.6 nm. Thicker films of Si and SiO gave spectra with rapidly decreasing backgrounds. The spectrum of the Si film shows a strong peak at 2060 cm^{-1}, and medium peaks at 890, 620 and 480 cm^{-1}. The spectrum of the SiO film shows intense peaks at 2190 and 880 cm^{-1}, and a medium peak at 690 cm^{-1}. The features of the spectrum of SiO agreed well with those of the spectra previously measured.[2-4] The agreement shows that our procedures for preparing the junctions and measuring the tunneling spectra are suitable for thin films of Si and SiO. These peaks in the tunneling spectra are due to vibrational modes of species in the thin films of Si and SiO.

The infrared and Raman spectra of the hydrogenated amorphous silicon films made by reactive sputtering of Si in hydrogen[9] and plasma decomposition of SiH_4[10] have the strong stretching (ν) modes of the SiH, SiH_2, and SiH_3 species at 2000 - 2140 cm^{-1}. Their deformational modes lie between 600 - 900 cm^{-1}. The peak at 2060 cm^{-1} in the tunneling spectrum corresponds to the νSiH and νSiH_2 mode. The shoulder at 2180 cm^{-1} seems to correspond to the νSiH_3 mode. The peak at 890 cm^{-1} is due to the scissoring (γ) mode of SiH_2. The peak at 620 cm^{-1} is due to the

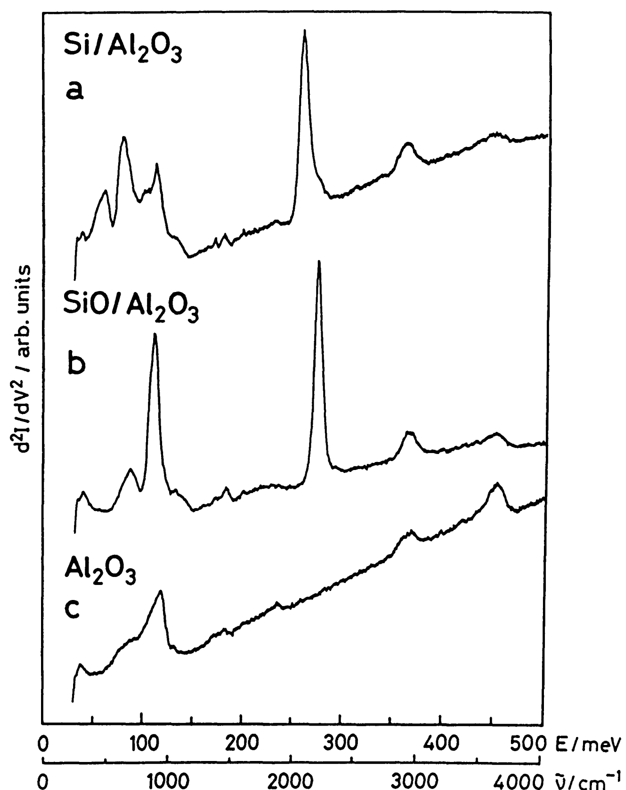

Fig. 1. Tunneling spectra of junctions of (a) $Pb/Si/Al_2O_3/Al$, (b) $Pb/SiO/Al_2O_3/Al$, and (c) $Pb/Al_2O_3/Al$ prepared at 3.4, 8.2, and 7.0×10^{-6} Torr, respectively.

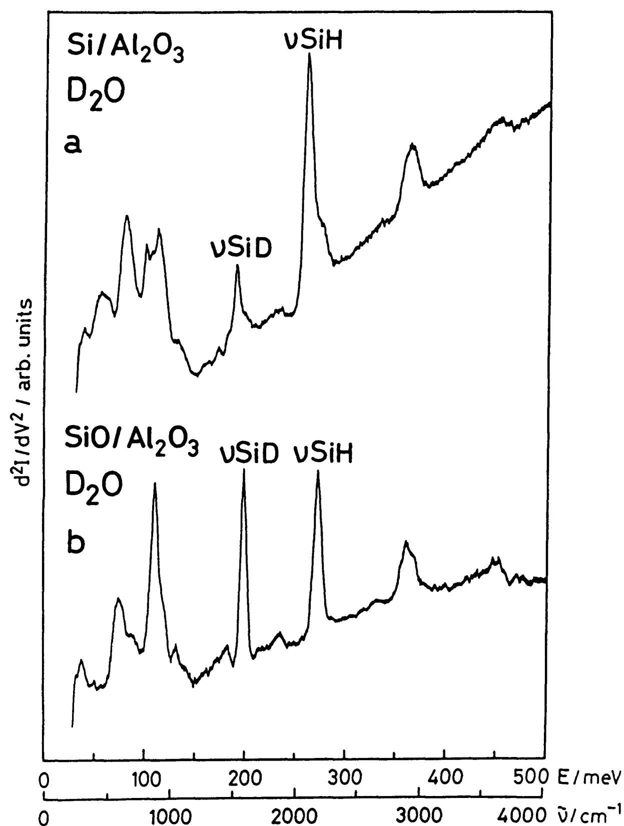

Fig. 2. Tunneling spectra of junctions of (a) $Pb/Si/Al_2O_3/Al$ and (b) $Pb/SiO/Al_2O_3/Al$ prepared at 2.0 and 2.4×10^{-5} Torr of D_2O, respectively.

bending (ρ) mode of SiH and the rocking (ρ) mode of SiH_2. The peak at 480 cm^{-1} is caused by the νSi-Si mode. The tunneling spectrum of the silicon film prepared by the vacuum evaporation of Si indicates the presence of SiH, SiH_2, and SiH_3 species. These SiH_{1-3} species found in the tunneling junction are equivalent to those in the hydrogenated amorphous silicon films.[9,10]

The vibrational spectra of the hydrogenated amorphous silicon film containing oxygen have the νSiH peak of the $Si_{3-x}O_xSi$-H (x=1-3) species in the 2100 - 2250 cm^{-1} region.[11] Its frequency is shifted from 2000 cm^{-1} as in the hydrogenated amorphous silicon film. This is due to an induction effect associated with the oxygen atom being bonded to the same silicon atom. The bending (ρ) peak of the SiH species lies in the 630 - 875 cm^{-1} region. The Si-O-Si moiety has its stretching mode at 940 cm^{-1}, and in-plane (scissoring:γ) and out-of-plane bending mode at 650 and 500 cm^{-1}, respectively. There is no evidence for the existence of the OH group.[11] The peaks at 2190 and 880 cm^{-1} in the tunneling spectrum of the SiO film correspond to the νSiH and ρSiH mode of the SiO_2Si-H species,[11] respectively. The peaks at 1040 and 690 cm^{-1} are caused by the νSi-O-Si and γSi-O-Si mode, respectively. The tunneling spectrum of SiO also shows the SiH species, however, the monohydride is formed in its thin evaporated film. Oxygen atom being bonded to the silicon atom may increase the solubility of hydrogen in the monohydride geometry in the amorphous silicon film as in the case of the oxygen containing hydrogenated amorphous silicon.[11]

In order to ensure the presence of silicon hydrides and to clarify the mechanism for their formation, the Si and SiO films were prepared in the atmosphere of D_2O. The tunneling spectra are shown in Fig. 2, and their peak positions are given in Tables 1 and 2. Also given are the peak positions obtained for the spectra of the Si and SiO films prepared in high vacuum. The spectrum of the Si

Table 1. Vibrational frequencies (cm^{-1}) and mode assignments for SiH species in evaporated Si film measured by IETS.

Vacuum[a]	D_2O[b]	Assignment
2180 sh	2180 sh	νSiH_3
2060 s	2070 s	νSiH and νSiH_2
	1580 sh	νSiD_3
	1500 m	νSiD and νSiD_2
890 m b	880 m b	γSiH_2
830 sh	840 sh	ωSiH_2
	790 m	γSiHD
620 m b	630 m b	ρSiH and ρSiH_2
480 m b	440 m b	νSi-Si

a) Prepared at 3.4 × 10^{-6} Torr.
b) Prepared at 2.0 × 10^{-5} Torr of D_2O.

Table 2. Vibrational frequencies (cm^{-1}) and mode assignments for SiH species in evaporated SiO film measured by IETS.

Vacuum[a]	D_2O[b]	Assignment
2190 s	2190 s	νSiH
	1590 s	νSiD
1040 w b	1050 w b	νSiOSi
880 s	880 s	ρSiH
690 m b	700 sh	γSiOSi
	590 m b	γSiOSi and ρSiD

a) Prepared at 8.2 × 10^{-6} Torr.
b) Prepared at 2.4 × 10^{-5} Torr of D_2O.
s:strong, m:medium, w:weak, sh:shoulder, b:broad, ν:stretch, γ:scissors, ω:wag, ρ:bend or rock.

film prepared at a pressure of 2.0 × 10^{-5} Torr of D_2O shows the strong and medium peak at 2070 and 1500 cm^{-1}, respectively. The peak at 1500 cm^{-1} lies at the expected position (2070/1500 = 1.38) and clearly shows the formation of the SiD and SiD_2 species. The spectrum of the SiO film prepared at a pressure of 2.4 × 10^{-5} Torr of D_2O also shows the SiD peak at 1590 cm^{-1} (2190/1590 = 1.38). The spectrum of the junction doped with D_2O after completing the films of Si and SiO gave no SiD peak. The transmission infrared specrtra of the evaporated thick (about 500 nm) Si and SiO films on KBr pellets measured with a Shimadzu FTIR-4200 also show the corresponding SiH peaks at 2100 - 2250 cm^{-1}. These facts show that the hydrides are formed mainly during the evaporation from reaction with the residual water molecules in the vacuum system, agreeing with those for the SiH formation of SiO observed by Mazur and Hipps.[3,4]

The evaporated silicon film has been shown to be in an amorphous state and to have deficiencies (dangling bonds).[12] The density of the dangling bonds was measured from the spin concentration by electron spin resonance. These dangling bonds are closely related to the properties of the films. From the present study, it appears that some of the dangling bonds in the evaporated Si and SiO films are reduced by the reaction with residual water molecules to form the SiH species. Similar SiH formation has been reported for the tunneling junctions of SiO,[2-4] SiO_2,[5] and the oxidized Si wafers.[6,7] The present work is the first attempt to measure and analyse the tunneling spectra of both Si and SiO films. The comparisons made possible by this two-pronged approach provide a clear picture of the surface species. Further investigations on the properties of the thin films of evaporated Si and SiO are now in progress.

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