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Anomalous Dielectric Behavior in Nanometer-Sized Amorphous Silicon Nitride*

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An anomalous dielectric behavior in nanometer-sized amorphous silicon nitride is reported. The dielectric constant of nanometer-sized amorphous silicon nitride has strong dependence on frequency at room temperature (RT), which is completely different from the conventional coarse-grain silicon nitride. The maximum of the dielectric constant of nanometer-sized amorphous silicon nitride at RT is about 40 times larger than that of the conventional silicon nitride. The anomalous dielectric behavior is explained by a kind of mechanism of polarization, that is, interfacial polarization.

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The dielectric constants of conventional amorphous and crystalline Si_3N_4 are respectively about 8.66 and 8.36 at room temperature (RT).[1] Generally, the real part ε' of complex dielectric function (DF) in amorphous or crystalline Si_3N_4 has no dependence on frequency at RT.[1] However, there have yet been no reports found concerning the dielectric constant of nanometer-sized amorphous silicon nitride. The aim of this letter is to show a dielectric behavior of nanometer-sized amorphous silicon nitride.

The nanometer-sized amorphous silicon nitride bulk was synthesized by a two-step procedure.[2] The specimen was compacted under a pressure of 1.12 GPa for 3 min to form a disc shape specimen with 12 mm in diameter and approximately 0.6 mm in thickness. In the process of compaction, no binder was used. Before the measurements were made, all samples underwent bake treatment at 150°C in the vacuum of 10^{-5} Torr for 30 min to eliminate absorbed moisture and surface contamination.

The dielectric measurement at RT were performed in DP II dielectric device.[3]

Figure 1 shows the frequency dependence of ε' at RT in the as-compacted specimen and the specimens sintered at different temperatures. Curve *a* corresponds to the result of the as-compacted specimen. The average size of the grains observed on TEM was 15 nm as shown in Fig. 2. The x-ray diffraction spectrum indicates that the specimen is in amorphous state as shown in Fig. 3(a). Within the range from 10 Hz to 1 kHz, the ε' is much higher than that of Si_3N_4 obtained by the conventional method and it decreases rapidly with increasing frequency. When $f > 1$ kHz , ε' remains almost unchanged with increasing frequency, only when $f > 30$ kHz, does ε' fall slightly. Curve *a* indicates that the ε' of nanometer-sized amorphous silicon nitride at RT has a strong dependence on frequency when $f < 1$ kHz, whereas it is almost independent of frequency when $f > 1$ kHz.

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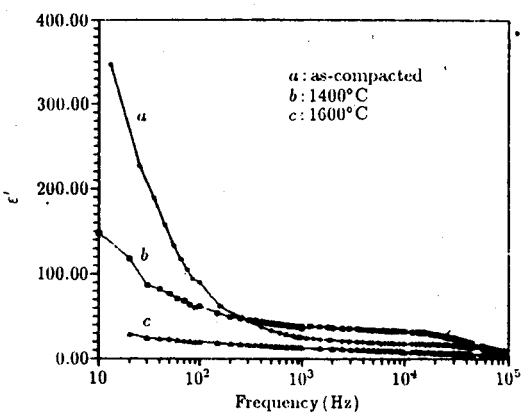

Fig. 1. Frequency dependence of ε' at RT for nanometer-sized amorphous silicon nitride samples sintered at the different temperatures.

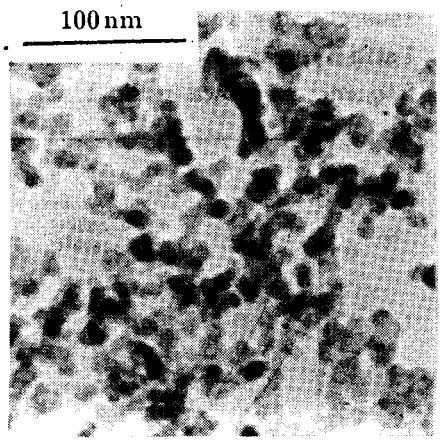

Fig. 2. TEM micrograph of the as-compacted sample.

Curve b refers to the result of the specimen sintered at 1400°C under a pressure of 1 atm N_2, TEM observation indicates that particles grains have grown to an average of 40 nm.[2] The x-ray spectrum illustrates that the specimen have transformed into a crystalline state as shown in Fig. 3(b). When $f < 1$ kHz, the ε' is much higher than that of the conventional CVD-Si_3N_4, but decreases more gradually compared with curve a. With increasing frequency, ε' falls rapidly. When frequency is between 1 and 20 kHz, ε' does not vary. When $f > 20$ kHz, ε' declines, but the declining tendency is relatively weak.

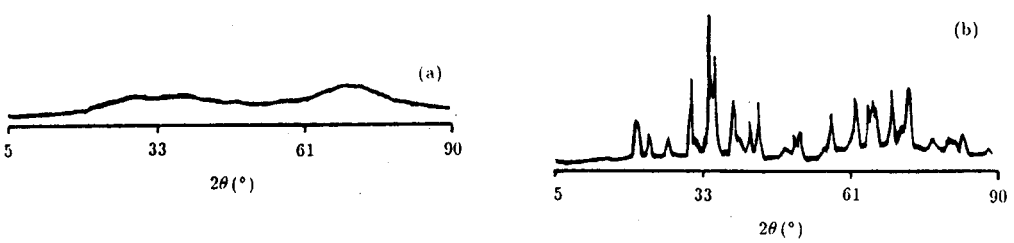

Fig. 3. (a) The x-ray diffraction pattern of the as-compacted sample. (b) The x-ray diffraction pattern of the sample sintered at 1400°C under the pressure of 1 atm N_2 after compaction.

Curve c gives the result of the sample sintered at 1600°C under a pressure of 1 atm N_2. By TEM, the average size of the grains was determined to be 1 μm.[2] From curve c, it can be seen that the ε' is much smaller compared with curves a and b when $f < 1$ kHz. When $f > 1$ kHz, ε' is almost independent of frequency. Compared with the conventional CVD-Si_3N_4, there is little difference.

Figure 4 displays the frequency dependence of RT ε'' in the as-compacted specimen and the specimens sintered at different temperatures. Curve a corresponds to the result of the as-compacted specimen. The curves b and c correspond to the results of the sample sintered at

1400°C under a pressure of 1 atm N_2 and the sample sintered at 1600°C under a pressure of 1 atm N_2, respectively. The changing patterns of ε'' with frequency is similar to that of ε' with frequency as shown in Fig. 1.

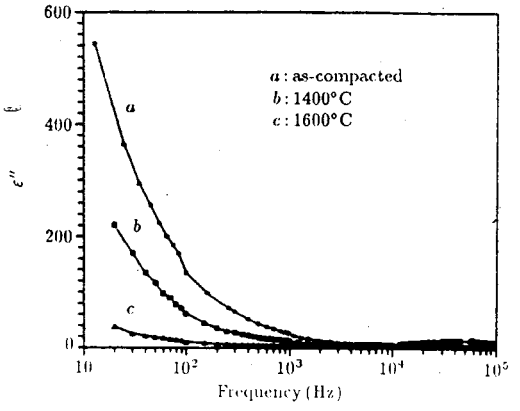

Fig. 4. Frequency dependence of ε'' at RT for nanometer-sized amorphous silicon nitride samples sintered at the different temperatures.

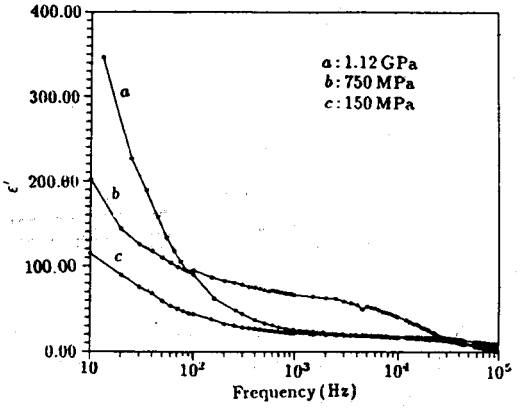

Fig. 5. Frequency dependence of ε' for the nanometer-sized amorphous silicon nitride samples compacted under different pressures.

Figure 5 shows the frequency dependence of ε' at RT for the specimens compacted under different pressures. Curve a is identical to curve a in Fig. 1, which shows the result after compaction for the specimen formed under a pressure of 1.12 GPa. Curve b shows the result of the specimen compacted under a pressure of 750 MPa. When $f < 1$ kHz, ε' is small compared with curves a, but is much higher than the conventional CVD-Si_3N_4. Along with the increase of frequency, ε' falls rapidly. Within the range from 1 to 20 kHz, the ε' changes a little but maintains a value of about 70. From 20 to 60 kHz, ε' also falls with increasing frequency. When $f > 60$ kHz, ε' is almost independent on the frequency. Curve c illustrates the result of the specimen fabricated under a pressure of 150 MPa. When $f < 1$ kHz, ε' is much smaller compared with curves a and b and decreases slightly with increasing frequency. When $f > 1$ kHz, ε' has no dependence on the frequency and there is no distinct difference compared with the conventional CVD-Si_3N_4.

We also measured the frequency dependence of ε' at RT for the specimens compacted under different pressures. The changing patterns of ε' with frequency is similar to that of ε' with frequency as shown in Fig. 5. According to the dielectric theory, a dielectric possesses strong dielectric performance in presence of electric field only when all dipoles have nearly the same orientation. Therefore, crystalline solids with the regular atomic arrangement possess strong dielectric performance in the presence of electric field, whereas amorphous material does not have strong dielectric performance because of the disordered structure. But our experimental data indicate the ε' in nanometer-sized amorphous silicon nitride is much high when $f < 1$ kHz. The maximum ε' can approach about 380, even though the structure of the nanometer-sized amorphous material is more random than that of the amorphous material.[4] The phenomenon displayed by a nanometer-sized material silicon nitride with a highly disordered structure can not be explained by conventional theory.

We suggest that this novel phenomenon may be related to a mechanism of polarization which is special to the nanometer-sized material—interfacial polarization (IP). IP is formed by the defect of dipole moment which is situated in the interface between adjacent particles. When loose powder is compacted into a solid specimen, the interface can be considered to consist of structural defects, such as a large number of unsaturated dangling bonds and microporosities, which can trap a large amount of space-charge. The number of dipoles is very large due to its very high ratio of interfacial volume . This would result in a large dipole moment in presence of electric field. This polarization possibly involves the hopping movement of captive space-charge, so the relaxation time is very long, and strong dielectric dependence can be exhibited only at low frequency ($f < 1\,\mathrm{kHz}$). Due to this type of special interfacial structure, a material originally with weak or without dielectric response may become strong dielectric after being nanometer-sized.

When $f < 1\,\mathrm{kHz}$, the interfacial polarization can follow the frequency. But when $f > 1\,\mathrm{kHz}$, the interface response can not follow the frequency and so does not play a major role in the polarization. Therefore, at a high frequency, the dielectric behavior exhibits independence of frequency. With the sintering temperature increasing, the grains become large, so the interfacial volume ratio and the distortion of the interface decrease, and the dielectric relaxation time quickly falls. With the fabricating pressure decreasing, the distortion of the interface becomes less obvious, and the dielectric constant also declines.

The ε'' represents the dielectric loss. In the presence of electric field, dipoles need certain energy to orient the direction of the dipoles to the direction of the applied electric field. Of course, the higher the number of dipoles, the more energy is needed. Therefore, the dielectric loss is higher when the number of dipoles increases. With the sintering temperature increasing and the fabricating pressure decreasing, the number of dipoles decreases, the dielectric loss decreases.

When $f > 1\,\mathrm{kHz}$, the dielectric response cannot follow the change of frequency. The dielectric loss does not change with frequency which is consistent with the changing pattern of ε'.

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