

Surface metallization of PTFE and PTFE composites by ion implantation for low-background electronic substrates in rareevent detection experiments

Shao-Jun Zhang¹ · Yuan-Yuan Liu¹ · Sha-Sha Lv¹ · Jian-Ping Cheng¹ · Bin Liao¹ · Pan Pang² · Zhi Deng³ · Li He⁴

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Abstract Polytetrafluoroethylene (PTFE) is a low-background polymer that is applied to several applications in rare-event detection and underground low-background experiments. PTFE-based electronic substrates are important for reducing the detection limit of high-purity germanium detectors and scintillator calorimeters, which are widely applied in dark matter and $0\upsilon\beta\beta$ detection experiments. The traditional adhesive bonding method between PTFE and copper is not conducive to working in liquid nitrogen and extremely low-temperature environments. To avoid adhesive bonding, PTFE must be processed for surface metallization owing to the mismatch between the PTFE and copper conductive layer. Low-background PTFE matrix composites (m-PTFE) were selected to improve the electrical and mechanical properties of PTFE by

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Yuan-Yuan Liu yyliu@bnu.edu.cn

Sha-Sha Lv lvss@bnu.edu.cn

- ¹ College of Nuclear Science and Technology, Beijing Normal University, Joint Laboratory of Jinping Ultra-low Radiation Background Measurement of Ministry of Ecology and Environment Beijing Normal University, Key Laboratory of Beam Technology of Ministry of Education, Beijing Normal University, Beijing 100875, China
- ² Beijing Radiation Center, Beijing 100875, China
- ³ Department of Engineering Physics, Key Laboratory of Particle and Radiation Imaging of Ministry of Education, Tsinghua University, Beijing 100084, China
- ⁴ Joint Research Center, Nuctech Company Limited, Beijing 100084, China

introducing SiO₂/TiO₂ particles. The microstructures, surface elements, and electrical properties of PTFE and m-PTFE were characterized and analyzed following ion implantation. PTFE and m-PTFE surfaces were found to be broken, degraded, and cross-linked by ion implantation, resulting in C=C conjugated double bonds, increased surface energy, and increased surface roughness. Comparably, the surface roughness, bond strength, and conjugated double bonds of m-PTFE were significantly more intense than those of PTFE. Moreover, the interface bonding theory between PTFE and the metal copper foil was analyzed using the direct metallization principle. Therefore, the peel strength of the optimized electronic substrates was higher than that of the industrial standard at extremely low temperatures, while maintaining excellent electrical properties.

Keywords Surface modification · Polytetrafluoroethylene · Ion implantation · Surface metallization · Low temperature resistance

1 Introduction

The direct detection of dark matter and neutrinoless double-beta $(0\upsilon\beta\beta)$ decay experiments are listed as rareevent detection experiments because dark matter has an extremely small interaction cross section with the detector medium, and $0\upsilon\beta\beta$ has a significantly long half-life. In the rare-event detection experiment, the particles causing the environmental background were mainly cosmic ray muons, gamma rays, electrons, and neutrons. The cosmic rays and cosmogenic radionuclides generated by cosmic ray activation, natural radioactivity, target materials, shielding materials, and electronic components can lead to the detectors responding to these as background events. The following measures are undertaken to reduce the environmental background [1]: (1) building a deep underground laboratory to reduce the cosmic ray background, (2) composite shielding to establish a clean experimental space and reduce the background of radon and its daughters, such as water, lead, high-purity oxygen-free copper, polyethylene, and liquid argon. (3) minimizing the radiation background caused by surrounding materials through material radioactivity screening and control. Therefore, strict requirements for low-background materials, environmental background suppression, long-term stability of detectors [2–4], and signal readout cables have been proposed to increase the sensitivity of rare-event detection experiments.

Liquid nitrogen or liquid argon with low atomic numbers are commonly used as coolants [5] and for detector γ ray shields in rare-event detection experiments. For the Majorana experiment [6], a low temperature thermostat was used to control the experimental temperature lower than 100 K, and it obtained a background level of approximately 0.1 cpkkd (count per kg keV day) in the energy region of 5 keVee. The cryogenic underground test (CUTE) [7] facility focused on cryogenic germanium detectors (10 mK) for the super cryogenic dark matter search (SuperCDMS). For the GERmanium detector array (GERDA) experiment [8], a bare high-purity germanium detector was directly immersed in 70 tons of liquid argon through a stainless steel chain. Cuflon (a commercial copper foil composed of polytetrafluoroethylene (PTFE) and copper) was used as an electronic substrate in the GERDA experiment, and the radioactivity was controlled within the μ Bq level. For the China dark matter experiment (CDEX) [9], we operated 10 kg of high-purity germanium cooled by liquid nitrogen for dark matter detection experiments. For the next phase, the 50 kg germanium detector array was directly immersed in liquid nitrogen. To transmit the extremely weak rare-event signal obtained by the detector to the subsequent amplification circuit, the technical difficulties and challenges need to be solved under the direct cooling operation of liquid nitrogen, such as external cable creepage, short circuiting, the instability of the preamplifier signal caused by the local boiling of liquid nitrogen. Therefore, a crucial problem in rare-event detection experiments is ensuring the normal operation of key electronic substrates in a liquid nitrogen environment or at temperatures lower than what the substates are exposed to in a nitrogen environment [10].

Previous experiments regarding rare-events have imposed strict requirements on the radioactive purity of component materials that are difficult to solve by shielding [11, 12]. A circuit board is usually placed near the detector to transmit and amplify the important signal of the detector at extremely low temperatures. In addition, the circuit board in a single high-purity germanium detection unit accounts for approximately 0.2% of the quality, whereas it accounts for approximately 9% in the low-energy background through simulation estimates. This is a significant contribution to the background of detectors [13]. Therefore, the development of electronic substrates with a low background, good adhesion, and low-temperature resistance has meaningful benefits for rare-event detection experiments.

PTFE is a tetrafluoroethylene polymer and consists only of carbon (C) and fluorine (F) atoms, which has a significant advantage in terms of its low background and electrical properties. Thus, PTFE-based electronic substrates have become the preferred choice for circuit boards and cables in rare-event experiments, most of which need to be immersed in liquid nitrogen or liquid argon with the detector. However, PTFE is also known for its chemical inertia and has considerable defects, such as poor adhesion, poor mechanical properties, and a high coefficient of thermal expansion. The adhesives used for the electronic substrates may fail due to the interlayer stress difference at extremely low temperatures.

For the ion-beam modification of PTFE [14], ion beams can improve the adhesion of PTFE by etching, activating, and crosslinking. The modification effect of ion-implanted PTFE [15–27] follows this basic principle: The energy loss process of ions implanted into a polymer is mainly a nuclear stopping process and an electron stopping process. Interacting between the ion and target nuclei (screened) in a nuclear stopping process will lead to atomic collisions and vacancies, owing to the long distance between the molecular chains in the polymer. In addition, the chain scission of polymer molecules is largely a consequence of a nuclear stopping process. The interaction between the ion and target electrons in an electron-stopping process causes atomic ionization and electron excitation, which leads to the production of free groups and free bonds. Thus, the cross-linking and activation of polymer molecules are primarily led by an electron-stopping process. The nuclear stopping and electron stopping processes may be competitive, and their yields can be related to the linear energy transfer (LET) [28]. Most atomic displacements of nuclear collisions occur independently in the PTFE. With the large free volume of PTFE and the long distance between the molecular chains, chain scission and material loss are the main reactions under ion irradiation.

The excellent electrical properties of PTFE are attributed to its dielectric constant and dielectric loss. The dielectric constant is small and stable over a wide frequency range. The dielectric loss is also extremely small to protect the integrity of the signal, which is critical for rareevent experiments. Although PTFE-based substrates are widely applied, the literature regarding adhesive-free flexible PTFE-based electronic substrates is limited owing to trade secrets. Studies regarding the electrical properties of ion-beam-modified PTFE often focuses on superior surface conductivity, such as microwave substrates or triboelectric nanogenerators [29]. However, PTFE is required not only to maintain excellent insulation as a dielectric, but also to closely combine with metal copper in electronic substrates. Nobuyuki et al. [30] achieved cluster copper metallization on PTFE surfaces by atmospheric-pressure plasma liquid deposition; however, the electrical properties were not tested. Direct metallization on the PTFE surface for electronic substrates has rarely been studied.

According to the basic theory of the bonding force, the usual surface characterization factors of ion-beam modification include increasing the surface roughness [23, 24] and surface energy [25], addition of surfactant groups [26], enhancement of surface hydrophilicity [31], and cross-linking [32]. Bikerman proposed the weak boundary layer theory [33] in 1961. A weak joint was considered to exist in a bonding system. The low cohesion strength constitutes a "weak boundary layer (WBL)", which causes the binder system to break under an external force lower than the expected bonding strength. Although controversial, WBLs have been confirmed to exist on polymer surfaces, and a polymer-metal interface is layered owing to polymer cohesion failure [34, 35].

PTFE is a typical chain scission polymer under irradiation, and the interaction between the molecular chain and activated group is restricted to the outweighs of 90% crystallinity. The high linear thermal expansion coefficient of PTFE in the z-axis direction (CTE > 100 ppm/ °C) is also a significant disadvantage for metallization applications. Therefore, the incorporation of micron or nanofiller materials into PTFE is important for improving PTFE. SiO₂/TiO₂ particles are widely used in PTFE-based substrates to improve the coefficient of thermal expansion and the friction resistance of PTFE. The introduction of particles can improve irradiation resistance, reduce crystallinity, improve the chemical reaction performance under ion implantation, and maintain low dielectric loss [36]. In this study, both PTFE and m-PTFE (PTFE matrix composites with SiO_2/TiO_2 particles) were used to prepare electronic substrates.

Nickel (Ni) metal vapor vacuum arc (MEVVA) ion implantation and magnetic filtered cathodic vacuum arc (FCVA) metal particles were used as transition layers in this study to prepare PTFE electronic substrates with excellent adhesion [37]. We will further explore the influence of Ni ion implantation on the m-PTFE surface modification and measure the adhesion strength compared to that of PTFE. Simultaneously, the principle of direct metallization of the PTFE surface was explored in liquid nitrogen. PTFE and m-PTFE electronic substrates have excellent electrical properties and high adhesion, which can meet the requirements of low-background and extremely low temperature-resistant electronic substrates for rare-event detection experiments.

2 Methods and characterization

2.1 Sample preparation

Low-background PTFE and m-PTFE thin films were used, which has ultra-low contents of uranium and thorium elements, as measured by inductively coupled plasma mass spectrometry. After ultrasonic cleaning with alcohol and acetone for 10 min, the films were oven-dried at 60 °C for 1 h. Subsequently, PTFE and m-PTFE were modified successively in the special plasma etching-MEVVA-FCVA all-in-one ion beam and electroplating equipment. The vacuum during processing was maintained below 3 mPa. Figure 1 demonstrates the specific steps of the sample preparation. The corresponding sample names obtained in each step are listed below.

Step 1 Ar gas plasma etching. PTFE-A and m-PTFE-A were obtained after cleaning and etching the surface of the PTFE and m-PTFE films with a plasma power of 1000 W for 5 min.

Step 2 MEVVA ion implantation. The surfaces of PTFE-A and m-PTFE-A were treated by metal Ni ion implantation with an energy of 8 keV, and the corresponding fluence was 6×10^{16} ion/cm² to obtain PTFE-AN and m-PTFE-AN.

Step 3 Ar gas plasma etching. The PTFE-ANA and m-PTFE-ANA were obtained by the same operation as in step 1, and the processing time was 2 min.

Step 4 Deposition of the nickel transition layer. A Ni layer with a thickness of 5 nm was deposited by FCVA to obtain PTFE-ANAN and m-PTFE-ANAN. The arc and magnetic filter currents were 100 and 2 A, respectively.

Step 5 Copper transition layer deposition. A Cu layer with a thickness of 24 nm was deposited using the same operation as in step 4 to obtain PTFE-ANANC and m-PTFE-ANANC.

Step 6 Electroplating treatment. Adhesive-free flexible copper clad laminate (FCCL) was prepared by cathodic electrolytic copper sulfate plating. The PTFE-FCCL and m-PTFE-FCCL were obtained using an electroplating current density of 10 mA/cm^2 and a deposition time of 60 min, respectively.

2.2 Characterization and electronical properties

A Hitachi S-4800 scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS) were



Fig. 1 (Color online) Fabrication schematic of electronic substrates

used to observe the surface morphology and elemental composition, respectively. Raman spectroscopy was performed at an excitation wavelength of 325 nm^{-1} . The combination of EDS and Raman spectroscopy clearly distinguished the sample elements and molecular bonds. The surface free energy (SE) was calculated from the contact angle of distilled water and n-hexane using a Data physics OCA 20 contact angle measuring instrument. Dielectric property measurements were conducted between the frequency range of 10^{-1} Hz and 10^{6} Hz using a Novocontrol Technologies Alpha-A high-performance frequency analyzer, which provides a low-temperature measurement environment with a temperature as low as 173 K. A 90° peel strength tester was used to measure the peel strength of the PTFE and m-PTFE FCCLs; the peeling force was maintained at a constant speed of (50 ± 5) mm/min.

3 Results and discussion

3.1 SRIM simulation

LET is defined as the energy absorbed per unit ion path length, which is expressed as eV/nm/ion or eV/nm. To better identify the patterns of LET, we selected different ions that were implanted in PTFE in previous studies [15–27] and set the implantation energy range to 1–30 keV. Thus, the nuclear LET and electronic LET were simulated by the stopping and range of ions in matter (SRIM), as shown in Fig. 2. Considering the overall trend of H, He, O, C, and Ni, we found that the nuclear LET decreased with an increase in the electronic LET. Owing to the small Rutherford cross section and momentum transfer of low-mass atoms, the nuclear stopping effect caused by the small atoms of H and He can be ignored. At the same



Fig. 2 (Color online) SRIM simulation of nuclear LET and electron LET of different ions with energies ranging between 1 and 30 keV; the red boxes indicate the selected ions with corresponding energies found in literature works

energy, a higher atomic mass resulted in a higher nuclear LET. However, with the increase in atomic mass, the increase in the nuclear LET was significantly greater than that of the electronic LET, which indicates that the polymer mainly undergoes chain scission reactions. Therefore, the energy selection for the ion implantation used to improve the adhesion of PTFE was relatively small.

High energies, such as in MeV electron beams, proton beams, or helium ion beams will promote the cross-linking and branching reaction on a PTFE surface, thus greatly enhancing the surface hardness and wear resistance; however, it will also accelerate aging. The basic principle of ion implantation on PTFE has been verified in a previous study. David et al. [21] found that a 5.5 MeV helium ion first leads to a chain scission of the polymer film at a low dose, which is followed by cross-linking/branching. The electronic LET of helium ions is 1500 times that of the nuclear LET. The nuclear LET of the 8 keV silver ion was 15 times higher than that of the electronic LET [17]. The silver ions at low doses remain to undergo cross-linking and oxidation reactions to promote the adhesion of the PTFE polymer. These two experiments proved that both the nuclear stopping process and the electron stopping process can lead to chain scission and cross-linking. The difference is that the nuclear stopping process mainly leads to chain scission, whereas the electron stopping process mainly leads to cross-linking. However, certain unique chemical and physical modifications remain. The surface roughness of PTFE after Ag⁺, Ar⁺, and C⁺ implantation decreased with increasing fluence, which is contrary to the modification performance of other ion implantations. In addition, although the ion fluence is an important factor, there are other factors related to the experimental equipment and environment.

3.2 Topographical characterization

Figure 3a–f demonstrates the surface morphologies of the samples before and after Ni ion implantation. Compared to PTFE, m-PTFE was smoother and flatter. The surface of PTFE-A was more uniform after treatment with Ar plasma, while m-PTFE-A presented broken holes owing to the poor combination of SiO₂/TiO₂ doping and PTFE. An apparent cross-linking state exists on the surface and longitudinal depth, and a microfiber interleaving morphology is observed on the outer layer. The m-PTFE-AN presented a stronger rupture and cross-linking morphology than that of PTFE-AN. The increased surface roughness and steepness are conducive to reducing the concentrated stress on the substrate surface, increasing the interlayer contact area and enhancing adhesion.

3.3 Chemical composition changes

An energy dispersion spectrum (EDS) was used to analyze the surface element distribution and relative atomic percentage content of the samples magnified 1000 times. Figure 4 demonstrates that the atomic percentages of PTFE and m-PTFE under each experimental step are generally similar. The oxygen (O), silicon (Si), and titanium (Ti) contents on the surface of the m-PTFE sample after different treatments were nearly the same. The percentage of F atoms on the surface increases, which is due to the surface degradation of PTFE into smaller molecules after ionbeam modification, thereby increasing the molecular density. The F atoms exhibit self-migration with low surface energies.

After Ni ion implantation in the experimental step 2, the content of C atoms in PTFE-AN increased (Fig. 4a), whereas the proportion of F atoms in PTFE-AN decreased, as shown in Fig. 4b. This indicates that a certain amount of F_2 , C_2F_4 , and C_2F_6 gases [38] may have been generated and diffused after Ni ion implantation. The fluorine-deficient state also promotes the generation of cross-linking and free radicals. The ratio of C and F atoms in m-PTFE-AN sharply decreased (Fig. 4a, b) with an increase in the atomic percentage of Ni (Fig. 4c) and Si/Ti/O (Fig. 4d). This is because the exposure of SiO₂/TiO₂ in m-PTFE-AN increased, and the ratio of the C/F atoms significantly decreased accordingly. Similarly, after the plasma etching in step 3, the atomic percentages of Si/Ti/O on the surface

Fig. 3 The SEM surface morphology of different PTFE and m-PTFE samples





Fig. 4 EDS of PTFE and m-PTFE samples: a Carbon, b Florine, c Nickel, d Oxygen, Silicon and Titanium of pristine/-A/-ANA/-ANA/-ANAN/-ANANC, corresponding to pristine production steps 1/2/3/4/5

of m-PTFE-ANA decreased, resulting in a corresponding increase in the proportion of the C/F atoms of m-PTFE-ANA, which presents an opposite trend to that of PTFE-ANA.

Owing to the sufficient metal carrier reaction between the Ni and SiO₂/TiO₂ in m-PTFE, the Ni content is consistent with that of the Si/Ti atoms. In addition, there are more holes in the m-PTFE-AN film after Ni ion implantation, and fewer Ni and Cu atoms are deposited on the m-PTFE-ANANC surface than that on PTFE-ANANC. Finally, after Cu deposition by FCVA, the Ni atomic ratios of PTFE-ANANC and m-PTFE-ANANC demonstrated a relatively higher content with good mutual solubility between Ni and Cu.

3.4 Laser Raman

Figure 5 demonstrates the Raman spectra of the PTFE and m-PTFE samples. The excitation wavelength of visible light usually causes the fluorescence effect of the polymer; thus, an excitation wavelength of 324 cm^{-1} was selected. According to the relative studies [39, 40], we obtained the characteristic peaks of PTFE and m-PTFE, which are listed

in Table 1. The main Raman characteristic peak is the same as that of PTFE (Fig. 5a), and the Raman peak intensity of m-PTFE (Fig. 5b) is significantly reduced. Because the doping particles had little effect on the surface molecular structure of PTFE, we will focus on PTFE.

The peaks at 576 and 609 cm^{-1} were related to the vibration spectra of PTFE (as a band at 602 cm^{-1} in m-PTFE). The intensity at 576 cm^{-1} becomes weaker at high temperatures, while that at 609 cm^{-1} demonstrates the opposite trend. The peak at 609 cm^{-1} is caused by "disorder" and depends on low crystallinity. As shown in Fig. 5a, the Raman peak intensities were reduced for both the PTFE-A and PTFE-AN samples. Compared to the bands of the original PTFE, the plasma modification weakened the intensity of the corresponding peaks, which is consistent with the experimental results in Sect. 3.2. As the experiment progressed, the strength decreased at 576 cm⁻¹ and increased at 609 cm⁻¹. The original PTFE is a crystalline polymer with a long-range of order in its crystal structure; however, ion beam modification causes the polymer bonds to break and damages crystallinity.

The peaks at 1382 and 1584 cm^{-1} are the characteristic Raman peaks of the C atoms, which are called diamond-



Fig. 5 (Color online) Laser Raman spectra of the PTFE and m-PTFE samples

| Table 1 Raman shifts in PTFEand m-PTFE | | PTFE (cm^{-1}) | m-PTFE (cm^{-1}) | Assignment | Species |
|---|----|------------------|---------------------|---------------------|----------|
| | 1 | | 226, 489, 692, 1075 | SiO ₂ | |
| | 2 | | 168, 434, 902, 967 | TiO ₂ | |
| | 3 | 292 | 289 | $\gamma_t(CF_2)$ | A_1 |
| | 4 | 385 | 386 | $\delta(CF_2)$ | A_1 |
| | 5 | 576, 609 | 602 | | |
| | 6 | 736 | 734 | $v_s(CF_2)$ | A_1 |
| | 7 | 1216 | 1216 | $v_a(CF_2)$ | E_1 |
| | 8 | 1300 | 1298 | v(CC) | E_2 |
| | 9 | 1382 | 1380 | $v(CC)/sp^3$ carbon | A_1 |
| | 10 | 1584 | 1610 | $v(C=C)/sp^2$ | E_{2g} |

like and graphite-like peaks, respectively. The former is the symmetrical stretching vibration of C-C and represents amorphous carbon. The latter involves the in-plane stretching vibration of paired carbon sp^2 atoms, which exist at all sp^2 sites without sixfold rings. There is no clear pattern of regular hexagonal arrays of carbon atoms in PTFE, as in the case of graphite. The peak area and intensity ratio of sp^3/sp^2 were determined via peak fitting (Table 2). The plasma has a strong ability to etch and fracture the main chain, whereas the high energy provided to the substrate by Ni ion implantation promotes the generation of free radicals and improves the concentration of C=C. m-PTFE undergoes a reaction similar to that of PTFE by ion beam modification. The peak position of sp^3 did not change between PTFE and m-PTFE, whereas the concentration of v(C-C) significantly decreased. For sp^2 , the peak

position of m-PTFE shifted to a higher energy with an increase in concentration compared to PTFE. The change in the sp^2 structure in the Raman spectrum is significantly more apparent than that of sp^3 . In addition, the high excitation energy of ultraviolet light promotes the shifting of the peak position to a higher value. The concentration of the C=C conjugated double bonds in each sample was ranked as follows: m-PTFE-AN > m-PTFE > m-PTFE-A > PTFE-AN.

3.5 Contact angle and surface free energy changes

A CCD camera and computer software were used to accurately measure and calculate the contact angle (Fig. 6a, b) of n-hexane and water droplets, and the surface free energy (Fig. 6c-e) using the pedestal drop method.

| Table 2 sp^3 fit peaks and sp^2 fitpeaks* of PTFE/m-PTFE | Samples | PTFE-AN | m-PTFE | m-PTFE-A | m-PTFE-AN |
|---|----------------------------|------------------|------------------|------------------|-------------------|
| samples | sp^3/sp^2 | 53.6 | 4.3 | 1.7 | 1.3 |
| | Peak height of sp^3 band | $185(\pm 1.95)$ | $90.1(\pm 2.45)$ | $28.4(\pm 0.19)$ | $27.0(\pm 0.18)$ |
| | Peak height of sp^2 band | $3.45(\pm 0.15)$ | $20.8(\pm 0.17)$ | $17.0(\pm 0.30)$ | $21.5(\pm\ 0.17)$ |

*Gaussian, Lorentz, and Gaussian-Loren Cross fitting methods were used to obtain the appropriate data



Fig. 6 The water and n-hexane contact angle with error bars (a) and surface free energy (b) of the PTFE and m-PTFE samples

Because the substrates are polar materials, the error in their contact angle with the n-hexane polar material was greater than that of water. The water contact angle of the hydrophobic samples was greater than 90°, as shown in Fig. 6b. The hydrophobicity of the electronic substrate can help avoid the interference of the condensate when passing through different temperature regions. According to the analysis presented in Sect. 3.1, small protrusions and cracks are formed on the surface of the sample after Ar plasma etching, which is conducive to capturing a large amount of air, forming an air cushion, and reducing the actual solid-liquid contact area. All of these factors increased the water contact angle on the material surface. Ni ion implantation caused larger cracks and resulted in an increase in the contact angle between the sample and water/n-hexane. The m-PTFE samples maintained good hydrophobicity owing to the hydrophobic nature of the SiO₂.

The surface free energies of PTFE and m-PTFE were calculated using the OWRK model algorithm [41, 42] in the SCA software. The surface free energy (Fig. 6c) was composed of the dispersion force (Fig. 6d) and polarity (Fig. 6e). Ni ion implantation improved the surface energy of the polymers by increasing their polarity. For the nonpolar PTFE, the contact angle of n-hexane was sensitive to the change in the dispersion force (Fig. 6a, d), while the contact angle of the polar water was related to the elemental composition and surface morphology.

3.6 Peel strength

Interlayer adhesion is mainly composed of mechanical anchoring forces, intermolecular forces, and chemical bonds. The adhesion between PTFE and the metal layer was positively correlated with the surface roughness, polarity, and surface energy after ion implantation. m-PTFE-AN demonstrated higher adhesion to copper than PTFE-AN, whereas PTFE-AN had higher adhesion than PTFE-A and PTFE. Although several relative studies regarding the mechanical anchoring force and intermolecular force have been conducted, studies regarding the role of chemical bonds in promoting adhesion are limited. Fu et al. [43] used XPS to confirm that Ni plasma implanted by MEVVA can form metal fluoride ion bonds in PTFE: however, other metal fluoride states cannot be determined. Laser Raman spectroscopy demonstrated that the carbon $sp^2 \pi$ bond of PTFE significantly increased after Ni ion implantation. Because Ni is a transition metal, it accepts π bonding electrons through the dsp^2 hybrid orbital and then overlaps to form a σ three-center coordination bond (Fig. 7a) and an inner orbital complex. In addition, Ni can also be used to form an sp^3 external orbital complex with free F atoms (Fig. 7b). Furthermore, Cu is an adjacent transition metal element to Ni with the same orbital hybridization and complex morphology. Therefore, the binding force can be enhanced by achieving the corresponding coordination bonds. Because the force between the chemical bonds is significantly greater than the van der Waals force, the π bond is the main factor for PTFE adhesion. The C=C bond in PTFE is easily oxidized to carbonyl or carboxyl after encountering oxygen or water vapor, which enhances the binding force with metals [44].

The Cu/PTFE adhesion strength was maintained at approximately 0.7 N/mm despite after being soaked in liquid nitrogen for 7 days, while the untreated PTFE was completely incapable of bonding with the Cu film. The peeled surface appearance and surface element content of PTFE and copper foil were observed to determine the bonding principle of PTFE-FCCL. As shown in Fig. 8a, b, the tightly bonded PTFE and copper foil are strongly separated, leaving a damaged surface. This demonstrates that the PTFE-FCCL starts to tear from the interior of PTFE, which proves that PTFE is a polymer that is characteristic of cohesive destruction and delamination. The stripped surface and element content of PTFE-FCCL after being soaked in liquid nitrogen for 7 days are nearly the same as those of PTFE-FCCL, which indicates that PTFE-FCCL maintains good adhesion after being immersed in liquid nitrogen. Additionally, the internal stress of the interface layer did not change. The EDS spectrum demonstrates that only C/F elements are present on the stripping surface on the PTFE side, whereas C/F/Ni and



Fig. 8 SEM and EDS of the peeled surfaces of PTFE-FCCL. a SEM of the peeled surface on the PTFE side, b SEM of the peeled surface on the copper side, and c EDS of the peeled surface on the PTFE or

copper side of PTFE-FCCL or LN7; the LN7 is after soaking PTFE-FCCL in liquid nitrogen for 7 days

other elements are present on the stripping surface of the copper foil side (Fig. 8c). Ohkubo [45] proposed that a better WBL recovery for PTFE leads to a stronger adhesion. The PTFE surface forms a three-dimensional texture of the WBL under ion beam modification, and the transition layer fabricated by FCVA soaks into the WBL. The active reaction point gradually solidifies with the self-healing process of WBL, strengthening the adhesion between PTFE and the metal interface.

3.7 Dielectric property changes

The PTFE single polymer chain had a helical coil structure and was tightly packed into a hexagonal structure. The high dipole moments of the– CF_2 – units on the alternating carbon skeleton cancelled one another owing to their opposite vector directions, which resulted in the significantly low dielectric constant of PTFE. However, Ni ion implantation introduced polar bonds and destroyed the structural symmetry of PTEF, leading to a lack of offset of the dipole moment and an increase in the dielectric constant within a small range. m-PTFE remains to have a high degree of cross-linking, which hinders the movement of the SiO₂/TiO₂ particles, the dielectric constant of m-PTFE increased and the dielectric loss decreased.

The dielectric properties of the electronic substrates at 296 K, 273 K, and 173 K are shown in Fig. 9a. The dielectric constant increased from 1.2 (PTFE) to 1.6 (m-

PTFE) at 10^{6} Hz; however, the dielectric loss, which is important for the integrity of signal transmission, remained low. The m-PTFE pristine membrane had a better temperature coefficient of the relative permittivity than that of the pristine PTFE membrane. PTFE-AN is apparently more prominent after ion implantation, which indicates that PTFE-AN has strong adaptability at low temperatures. We also used a commercial electronic substrate with excellent dielectric properties at room temperature; the dielectric loss increased to 0.006 at 273 K and continued to increase to 0.047 at 173 K.

The alternating current (AC) conductivities of the PTFE and m-PTFE dielectrics at frequencies ranging from 10^{-1} to 10^{6} Hz at different temperatures are shown in Fig. 9b. The AC conductivity (> 10^{-6} S/cm) indicates that a conductive path may occur under an external electric field. Therefore, the conductivity of the samples demonstrated that excellent insulation was maintained at various temperatures.

4 Conclusion

The ion deposition transition layer and surface metallization of low-background PTFE and m-PTFE are processed by the ion-beam-modified all-in-one machine; the FCCL is then achieved by the deposition of electrolytic copper sulfate. The surface roughness and steepness of the membranes increased after ion implantation. Through Fig. 9 (Color online) a Electrical properties of PTFE and m-PTFE dielectric substrates at 10^6 Hz, and the b alternating current conductivity of PTFE and m-PTFE dielectrics against the frequency at different temperatures



experimental analysis, Ni ion implantation was found to mainly promote the generation of C=C conjugated double bonds and increase the water contact angle, polar force, and surface free energy. Ni ion implantation can help form an internal orbital coordination bond with the $sp^2 \pi - \pi$ bond of C=C in the form of dsp^2 . This coordination bond between the π - π bond and Cu is greater than the van der Waals force, which effectively improves the binding force. As the reaction points of the transition layer increase, the mechanical anchoring force between the interfaces and the penetration of Ni into the WBL are enhanced for substrate adhesion. The introduction of SiO₂/TiO₂ particles in m-PTFE caused the chemical reaction or physical properties to change by having a higher strength than PTFE after ion beam modification. The m-PTFE-FCCL has better adhesion and relatively excellent mechanical and electrical properties, without affecting the chemical structure and background of the membrane. Both PTFE-FCCL and m-PTFE-FCCL demonstrated good electrical properties and low-temperature resistance and thus can prospectively be applied in extremely low-temperature electronic substrates.

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