Enhancement of microwave absorption properties on modified kapton film by ion implantation process

S Purwanto¹, W A Adi¹ and Y Taryana²

¹Center for Science and Technology for Advanced Material -BATAN, Puspiptek Area, Tangerang Indonesia 1314
²Research Center for Electronics and Telecommunication – LIPI, Bandung Indonesia

Email : setyo_p@batan.go.id

Abstract. Kapton-polyimide films have been modified by using ion implantation of Fe and Gd ions at dose $1 \times 10^{17}$ ions/cm² and energy ions 30 keV. From X-ray diffractions (XRD) were verified the existence phases such as iron oxide, or Gd-oxide and graphitic carbon. Vibrating sample magnetometer (VSM) measurement the films showed a paramagnetic behavior. Microwave absorption (MWA) properties were measured by vector network analyzer (VNA) at X band range (8-12GHz). VNA measurement results showed the enhancement of MWA from -22dB for Kapton original film to -35dB for S11 vector direction and until -40 dB for S22 vector direction of modified Kapton film by Fe and Gd ions. It can be concluded that the nanostructure of embedded Fe-oxide or Gd-oxide nanoparticles on the near surface of Kapton film take a role and gives a rise the MWA properties of film.

1. Introduction

Research on Kapton-polyimide films $(C_{22}H_{10}N_2O_5)_n$ have many interest during recently decade. This kind of films was excellent thermal stability, chemical resistance and exceptional mechanical and electrical properties and many uses such in nuclear power plants, military aircraft and space shuttles [1, 2]. Ion implantation or irradiation is a powerful technique to modifying the films surfaces including electrical and magnetic properties [3]. Since modification due to ion implantation may be caused by two mechanisms: the doping effect and the bombardment effect. Therefore ion bombardment leads to significant change of the polymer structure as a substrate and can embed some impurity and fabricate a composite material. Implantation of metal ion to high fluence leads to the formation of nanoparticles [4]. There are some research about metal Fe, Co or Gd ions implanted into polymer films such as Polyimide (PI) or Kapton due to some physical properties such as Magnetoresistance [5], also modification electrical properties of polyimide (PI) by Xenon (Xe) ions [6]. Unfortunately the data related to microwave absorption properties have not been done yet. The aims of this research are to modify Kapton-polyimide film by using ion such as iron (Fe) or Gadolinium (Gd) and to investigate the relation between the existence of the phases, magnetic properties and microwave absorption.

2. Experimental

Pristine Kapton-polyimide $(C_{22}H_{10}N_2O_5)_n$ samples were purchased from Nilaco-Japan. The film thickness was 125 micrometer. Implanted ions of Gd and Fe were generated from Gd and Fe powder with purity 99.9%, respectively and purchased from Sigma-Aldrich. The 30 keV Gd and Fe ions were
implanted into Kapton-Polyimide films within area 3.0 × 3.0 cm², with fluences or doses 1 × 10¹⁷ ions/cm² and ion current densities (20 µA/cm² during t = 200 minutes). Implantation process has been done in the vacuum chamber by ion implanter at Center for Accelerator Technology-BATAN. The penetrating range of Gd and Fe ions into Kapton films was calculated to be 29.2 nm and 37.9 nm using the SRIM 2008 software. Verification of implanted samples were determined by means of X-ray diffraction (XRD) to verify the existence of carbon-rich phases, vibrating sample magnetometer (VSM) for M-H curve and vector network analysis (VNA) for microwave absorbance properties, respectively.

3. Results and discussions

3.1. Depth Distribution Simulation

Based on TRIM (the Transport of Ions in Matter) software calculation at the same energy ion 30 keV, only 39 nm and 29 nm at the near surface of film is supposed to be a layer strongly modified by the Fe ion and Gd ion bombardement, as shown in figure 1(a) and 1(b), respectively. V.N. Popok [7] reported that only light narrow near surface to ~25 nm strongly modified by the ion bombardment and comprising composite metal/polymer material without any damaged on the top film surface. Furthermore Khabulin, et al. [8] determined the existence of formation nanogranular magnetic of Fe with the sizes ranges of 60 nm into Kapton film.

![Figure 1. TRIM simulation for Fe ion 30 keV implanted into Kapton film, with ion range 39 nm depth (a) and Gd ion 30 keV with 29 nm depth (b).](image)

3.2. X-ray diffraction (XRD)

Since high doses of ion could promoted the formation of carbonaceous layer with the filling of metal factor up to 25% as reported by V.N. Popok [7], therefore post implanted Kapton-polyimide film exhibits a different XRD pattern as shows in figure 2 and figure 3. A new peak appears in the post implanted Kapton-polyimide XRD pattern at 2-Theta = 24.8° indicating the presence of a new lattice spacing with d=3.59 Å. This peak clearly corresponds to the carbonized film as reported by Chen, et al. [6]. Phase analysis of implanted samples has been performed with refinement of the XRD profile of the sample using GSAS software.
Figure 2. A typical refinement of the XRD pattern profile of Fe ion implanted Kapton film with phase identification, Kapton phase (black bar), graphitic Carbon phase (red bar) and Magnetite (blue bar).

The refinement results tabulated in table 1 and 2. In the case of Fe ion implanted Kapton film have three phases, namely a main phase of Kapton-PI 94.80 wt.%, a new phase of graphitic carbon 3.95 wt.% and Fe$_3$O$_4$ (magnetite) 1.25 wt.%, respectively.

| Name of compound | Phase | Mass fraction (wt.%) | Reference          |
|------------------|-------|----------------------|--------------------|
| Kapton           | C-H-O-N | 94.80                | ICDD-96-720-0096   |
| Carbon           | C     | 3.95                 | ICDD-96-120-0018   |
| Magnetite        | Fe$_3$O$_4$ | 1.25            | ICDD-96-900-2332   |

In the case of Gd ion implanted Kapton film also contain three phases of the Kapton-PI 95.83 wt.%, graphitic carbon 3.62 wt.% and Gd$_2$O$_3$ phase 0.55 wt.%, respectively.

| Name of compound | Phase   | Mass fraction (wt.%) | Reference          |
|------------------|---------|----------------------|--------------------|
| Kapton           | C-H-O-N | 95.83                | ICDD-96-720-0096   |
| Carbon           | C       | 3.62                 | ICDD-96-120-0018   |
| Gd-oxide         | Gd$_2$O$_3$ | 0.55                | ICDD-96-101-0339   |
Figure 3. A typical refinement of the XRD pattern profile of Gd ion implanted Kapton film with phase identification, Kapton phase (black bar), graphitic Carbon phase (red bar) and Gd$_2$O$_3$ phase (blue bar).

3.3. Magnetic properties

Magnetic properties of both samples of Fe and Gd ion implanted ions were measured by means of VSM method up to external field $H=1.0$ Tesla, as shown in figure 4(a) and (b). Characteristic of both samples were exhibit paramagnetic behavior, with $M_s=0.13$ emu/g and 0.04 emu/g for Fe and Gd ions implanted samples respectively. These properties are consistent with reports from Murmu, et al. [9] for Gd$_2$O$_3$ and Leveneur, et al. [10] for iron-oxide nanoparticles. Since the samples were implanted above percolation doses $5\times 10^{16}$ ions/cm$^2$ with high ion current densities (20 µA/cm$^2$ during $t=200$ minutes) which is a sort of equivalence to annealing. Therefore the granular metal layer on the top of surface film in the as-implanted sample consist of small oxides form of iron (Fe) or gadolinium (Gd) in paramagnetic state at room temperature [11]. The concentration for Gd-oxide compare to iron-oxide was lower due to the penetration depth of Gd ions shorter (only 29 nm) compare to Fe ions (39 nm), respectively. This data also is consistent with the results of the analysis phases of the XRD profile as tabulated in table 1 and 2.
Figure 4. Magnetization curve profile for iron ions implanted Kapton (a) Fe ions and (b) Gd ions implanted into Kapton at doses $10^{17}$ ions/cm².

3.4. Microwave absorption properties
Microwave absorbances of the samples were determined by VNA method and measure at range 8-12 GHz. In case of Kapton film, characteristic of reflection loss (RL) were shown maximum RL= -22 dB at 11.7 GHz, with three absorption frequency at 11.4 GHz, 10.0 GHz and 8.4 GHz. This properties are mainly come from dielectric loss of the pristine PI film. But, this characteristic were changed in post implanted Fe and Gd film as shown in figure 5. The optimum reflection loss in post implanted Kapton film has been increased to RL=-35 dB and resonance frequency shifted to 11.4 GHz. The frequencies of the RL peak move to the low frequency direction and the strength of absorption first frequency increases can be explained by the quarter wave theory [12]. This results were comparable to microwave absorbance of composites based on PANI or PET film [13]. We suggest paramagnetic nanogranular from implanted ion Fe and Gd at the near surface take a role in this phenomenon with form metal/polymer nanocomposite region, as well as the existence of a new phase carbonized film.

4. Conclusion
Low energy 30 keV Fe and Gd ions were implanted in Kapton-polyimide film at doses $1 \times 10^{17}$ ions/cm² to create the nanogranular magnetic composite material beside a new carbonized phase. Both modified Kapton film have paramagnetic properties at room temperature. The implanted Fe and Gd ions were distributed homogenous and forming iron-oxide and Gd-oxide compound. Enhancement of microwave absorbance in modified Kapton film were occurred with reflection loss (RL) = -35 dB compare to -22 dB for pristine Kapton-polyimide.
Figure 5. Vector Network Analysis profile for pristine Kapton-polyimide (red line) and post implanted Fe+Gd (blue-line)

References

[1] Simpler 2015 Electron. Lett. 51(2) 127
[2] Teber A, Unver I, Kavas H, Aktas B and Bansal R 2016 J. Magn. Magn. Mater. 406 228-32
[3] Popok V N. 2012 Rev. Adv. Mater. Sci. 30(1) 1
[4] Popok V N, Nuzhdin V I, Valeev V F and Stepanov A L, 2014 J. Mater. Res. 29 1-7
[5] Kharchenko A, Lukashevich M, Popok V, Khaibullin R, Valeev V and Bazarov V 2013 Part. Part. Syst. Char. 30(2) 180–4
[6] Chen T, Yao S, Wang K, Wan H and Zhou S 2009 Surf. Coat. Technol. 203 3718-21
[7] Popok V N 2014 Rev. Adv. Mater. Sci. 36(1) 1–12
[8] Khaibullin R I, Popok V N, Bazarov V V Zheglov E P, Rameev B Z and Okay C 2002 Nucl. Instrum. Methods Phys. Res., Sect. B. 191(1-4) 810–4
[9] Murmu P P, Kennedy J, Ruck B J, Markwitz A, Williams G V M and Rubanov S 2012 Nucl. Instrum. Methods Phys. Res., Sect. B 272 100–3
[10] Leveneur J, Waterhouse I N, Kennedy J, Metson J B and Mitchell D R G 2011 J. Phys. Chem. C 115 20978–85
[11] Rameev B, Okay C, Yildizm F, Khaibulin R I, Popok V N and Aktas B, 2004 J. Magn. Magn. Mater. 278 164
[12] Li L Z, Wei J Z, Xia Y H, Wu R, Yun C and Yang Y B 2014 Appl. Phys. Lett. 105(2) 022902
[13] Ni Q-Q, Zhu Y-F, Yu L-J and Fu Y-Q 2015 Nanoscale Res. Lett. 10(1) 174