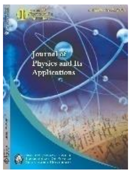
Journal of Physics and Its Applications

Journal homepage : https://ejournal2.undip.ac.id/index.php/jpa/index



Layer Deposition of Titanium Dioxide (TiO_2) Using Dc-Sputtering Method with Variation of Deposition Time: Study of Microstructure and Coating Hardness

Uli Aprilia Mukaromah[1], Wiwien Andriyanti[2], Heri Sutanto[1*], Nuha Nazilah Sahabudin[1]

[1]Department of Physics, Faculty of Science and Mathematics, Diponegoro University, Semarang, Indonesia
[2]PSTA BATAN, Jl. BabarsariPO BOX 6101 YKBB, Yogyakarta, Indonesia

[*)]Corresponding author: herisutanto@live.undip.ac.id

ARTICLE INFO

Article history:
Received: 20 September 2021
Accepted: 27 November 2021
Available online: 29 November 2021

Keywords:
Titanium dioxide
DC-Sputtering
Stainless Steel 316L
Hardness

ABSTRACT

The A thin layer of titanium dioxide has been deposited using the DC-Sputtering method at various time of deposition of 30 minutes, 60 minutes, 90 minutes, 120 minutes and 150 minutes. This study aims to grow a layer of TiO_2 on the surface of stainless steel 316L with a certain time variation to determine the characterization of the microstructure, hardness, and properties of the coating to the water contact angle. The XRD test results show that the titanium dioxide (TiO_2) thin layer has a TiO_2-monoclinicstructure corresponding to the planes (133), (133), (220), (133) and (133), while the crystallite size can be determined using Debye-Scherrer Equation were ~14.34318 nm, ~17.09422 nm, ~18.94568 nm, ~14.04389 nm, and ~7.90887 nm, respectively. The hardness value was obtained through the Vickers Hardness Test and it is known that the TiO_2 layer can increase the hardness value by ~48.175% with a maximum hardness value of 170.105 VHN at a deposition time of 90 minutes. Observations from the contact angle test can be seen that the TiO_2 layer is hydrophilic.

1. Introduction

Implant material is an important component of biomedical treatments such as fractures, reconstruction and joint replacement [1]. Materials used in the manufacture of implants are usually made of biomedical materials that have biocompatible properties, are not easy to corrode and are not toxic to the human body such as metallic materials or commonly called metal implants [2].

Metal implants material used in biomedical medicine depend on the function and quality of the material. The quality of the material can be seen from the value of high hardness, resistance to wear, resistance to corrosion, has a good compatibility value and so on. One of the metal materials that function as implants to replace the structure or function of human biological parts such as bones, kneecaps, wrists and the like is stainless steel type 316L. The use of 316L stainless steel is based on its affordable price, abundant availability, and biocompatible requirements [2]. Although 316L stainless steel biomaterials have higher hardness and corrosion resistance than other materials such as pure iron, 316L stainless steel has poor wear resistance values when compared to other biomaterials such as titanium. When a material wears out, the wear process causes the release of metal ions which can cause toxicity to the body and implant failure [3]. This makes 316L stainless steel biomaterials less than optimal for use for long periods of time and there is fear of side effects or failure in biomedical applications [4].

In overcoming the problem of wear resistance and increasing the hardness of the material, one way that is often done is to perform surface treatment on the surface of 316L stainless steel. Several materials have been used for the deposition process, namely $Zn(PO_3)_4$ [5], but this layer deposition process is constrained by the effectiveness of the layer as an orthopedic implant material, Zn-Al [6] has a hardness value that is not much different from the substrate.

TiO_2 is an important commercial material that is widely used in various fields of the industrial sector, biomedical treatment, medicine and others [7]. This material has outstanding mechanical properties, good hardness and wear resistance, and high corrosion resistance [8]. Another characteristic that proves that TiO_2 is resistant to corrosion can be observed from its reaction to liquids. TiO_2 when combined with urushiol compounds has excellent hydrophobic properties with a highwater contact angle, ranging from 146.1 ± 0.3° [9]. From several properties of TiO_2 material, this material has the potential as a deposition material which aims to increase the hardness, strength and hydrophobic properties of a material.

Several methods that have been used to deposit TiO_2 are sol-gel [10], but the weakness of this method is the difficult process and the results are not necessarily optimal, and the Hydrothermal method [11] but requires a relatively long layer growth time. One method that requires a relatively short time and produces a layer that has been proven to be optimal is the DC-Sputtering Technique [12]. This method is recommended because of the aspect of freedom in choosing and adjusting deposition conditions, it is important to optimize the TiO_2 layer and its interface [13].

In this study, surface treatment was carried out by depositing a thin layer of TiO_2 using the DC-Sputtering method with titanium targets and a mixture of argon and oxygen gases with the type of substrate used Stainless steel 316L.

2. Methods

The method used to deposit a thin layer of titanium dioxide was the DC-Sputtering method [12], but before going to this method the substrate must first go through a preparation process. In the preparation process, the substrate from 316L stainless steel, which was originally in the form of bars, was cut with a low speed diamond saw into a disc with a thickness of 2 mm and a diameter of 1.5 cm. The selection of the size adjusts to the place / holder that is on the DC-Sputteringmachine. Furthermore, the pieces of the test object were smoothed with emery paper from the size of 200 mesh to 2000 mesh and continued with polishing with auto sol paste and velvet cloth in order to obtain a completely smooth and even surface. To remove the emery paper powder and the remaining dirt on the surface of the substrate, the samples were washed with running water and detergent or alcohol and then dried using a hairdryer [12].

In the DC-Sputtering process, to obtain optimal conditions, various parameters have been carried out for the length of deposition time, namely 30 minutes, 60 minutes, 90 minutes, 120 minutes, 150 minutes. While other parameters are fixed, the ratio of Argon:Oxygen gas = 70:30, the distance between the electrodes is 4 cm, the electrode voltage is in the range of 4.4 kV ~ 4.6 kV, and the vacuum is in the range of 2.6 x 10-2~ 2.7 x 10-2 Torr [12].

The formed TiO_2 thin layer was characterized using X-ray diffraction with a CuKα radiation source (λ=1.54060Å) in the range of 2θ= 10 to 90°. The purpose of this characterization is to determine the crystal structure formed on the surface of the sample. These structures were identified using COD (Crystallography Open Database).

The crystallite size is determined using the following Debye-Scherrer equation.

$$D = \frac{K\,\lambda}{\beta \cos\theta} \tag{1}$$

The results of the modified Debye Scherrer equation are used to determine a crystal size value with D = crystallite size, K = crystal form factor (0.9-1), λ = X-ray wavelength (1.54056Å), β= value of Full Width at Half Maximum (FWHM) (rad), θ= diffraction angle(°). Meanwhile, to determine the hardness of the coating, the Vickers Hardness test instrument was used and the interaction of the layer with the liquid was obtained using the water contact angle test.

3. Results and Discussions

3.1.Deposition of $TiO_2$with DC-Sputtering method

The sample resulting from DC-Sputtering deposition is shown in Fig. 1. Fig. 1. (a) is a 316L stainless steel substrate that has not been coated with TiO_2, from the sample it can be seen that the color of the substrate is silver [12], like the color of stainless steel in general. Meanwhile, samples that have been deposited with a thin layer of TiO_2 are sample images shown by (b), (c), (d), (e) and (f). From these samples, it can be seen that visually differences in color on the surface of the substrate and the surface of the deposited TiO_2 thin layer can be seen with variations in the duration of 30 to 150 minutes. Visually, it can be interpreted that the TiO_2 layer gradually changes from what was previously sky blue (b), medium blue (c), medium blue with a goldenrod color blend (d), until finally changing to purple or medium orchid (e) and (f). The cause of the color change is the thickness of the layer which is related to the time of deposition. The phenomenon of these colors was also observed in the study of Lee et al., (2012) [14]. The process of growing a thin layer of titanium dioxide carried out by Andriyanti(2016) formed a thin layer of titanium oxide with a thickness of ±5 μm and the percentage of oxygen content deposited on the surface of the titanium specimen was 14.17% of weight [15].

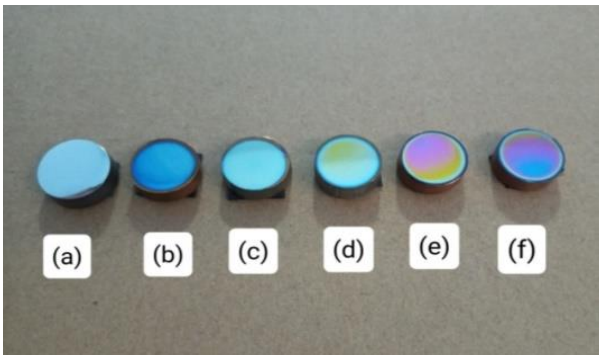


Fig. 1: Visual photos: (a) 316L stainless steel substrate, a thin layer of TiO2 deposited by the DC-sputtering method at various times (b) 30 minutes, (c) 60 minutes, (d) 90 minutes, (e) 120 minutes, (f)) 150 minutes.

3.2. X-Ray Diffraction

XRD spectra of 316L stainless steel substrate and TiO_2 thin film deposited in various variations of deposition time are shown in Fig. 2. Based on Fig. 2. information is obtained that in all material samples, a peak appears at 2-theta 44.16°. The peak is identical to the Fe phase based on the database (COD No. 96-901-3485), the peak of the spectrum is related to the plane (111). Meanwhile, at the 2-theta value of 50.86°, a peak that is identical to the Ni phase appears based on the database (COD No. 96-

901-2969) related to the field (240). The appearance of the Fe and Ni phases was due to the substrate used in TiO_2 deposition using 361L Stainless steel substrate. In accordance with research conducted by Hafizi et. al. in 2016 [16] stated that the chemical composition of 361L Stainless steel is composed of Fe less than 70%, Ni 10.1%, C 0.02%, Cr 17.2%, Mo 2.1%, Ti 0.003%, Al 0.002%, Nb 0.019% and several other elements [17].

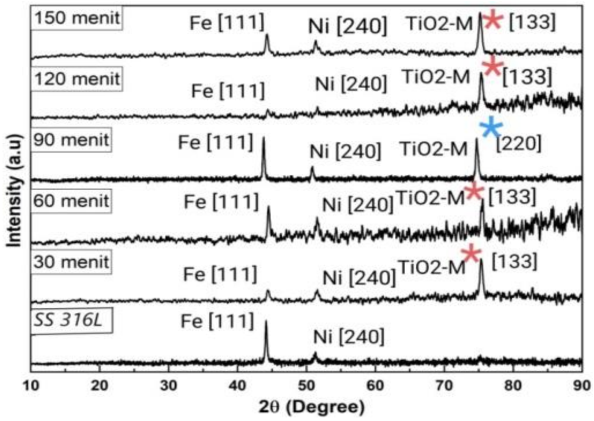


Fig. 2: XRD spectra of 316L stainless steel substrate and a thin layer of TiO_2 deposited in various variations of deposition time.

Fig. 2. also shows that TiO_2 compounds appeared in all samples deposited by the DC-Sputtering method with variations in the deposition time of 30, 60, 90, 120 and 150 minutes, respectively, producing XRD spectral peaks of 76.62°, 76.55°, 74.94°, 76.63°, and 76.63° which correspond to planes (133), (133), (220), (133) and (133), respectively. These peaks were analyzed referring to the monoclinic TiO_2 database (COD No. 96-110-0043) with cell parameters a= 5.8550, b= 9.3400, and c= 4.1420. From the five-time variations carried out, 90 minutes was the maximum for depositing TiO_2, apart from the identical angle to the database, another cause was the intensity and FWHM values which were the best when compared to the other four samples. Based on Fig. 2., it can be seen that the peak of TiO_2 which is marked by a blue star has a high intensity value and a low FWHM. Intensity values, FWHM (deg), lattice distance (nm) and crystallite size (nm) of 316Lstainless steel substrate and TiO_2 layer with variations in deposition time are shown in Table 1. Meanwhile, the peak marked with a red star is the opposite.

The difference in peak intensity and FWHM in each material sample shows certain characteristics of the material. The higher the intensity, the higher the crystallinity level [18]. As the material becomes more crystalline, the hardness level will also increase. This is in contrast to FWHM, the higher the intensity, the smaller the FWHM and the effect on the larger crystal particle size and tends to be more regular.

Table 1. Intensity value, FWHM (deg), distance between lattice (nm) and crystallite size (nm) of 316L stainless steel substrate and TiO_2 layer with variation of deposition time.

Sample	2θ (°)	Intensity (a.u)	FWHM (deg)	D (nm)
SS 316L	44.1654	1420	0.6065	11.93250
30 minutes	76.6238	1492	0.5891	14.34318
60 minutes	76.5597	1504	0.5000	17.09422
90 minutes	74.9458	2658	0.4512	18.94568
120 minutes	76.6329	1444	0.6086	14.04389
150 minutes	76.6317	1334	1.0807	7.908867

Based on the information on the crystallite size, intensity and FWHM (Table 1), when associated with the hardness value, it can be seen that as the crystallite size increases, the hardness of the material will also increase and have good crystallization regularity. To find out the hardness value, a hardness test is carried out.

3. 3. Hardness

The average hardness value of 316L stainless steel substrate is 122.83 VHN. While the test samples that have been carried out by the DC-Sputtering process with variations in time of 30 minutes, 60 minutes, 90 minutes, 120 minutes and 150 minutes, the hardness values are 124.34VHN, 13.78VHN, 170.105VHN, 148.44VHN, and 107.9 VHN. The maximum hardness value obtained is 170.105 VHN. If this hardness is compared with the hardness of the 316L stainless steel substrate of 12.83 VHN, there has been an increase in the hardness value of ~48.175%. The hardness values of 316L stainless steel substrate and TiO_2 thin films at various deposition times are shown in Fig. 3.

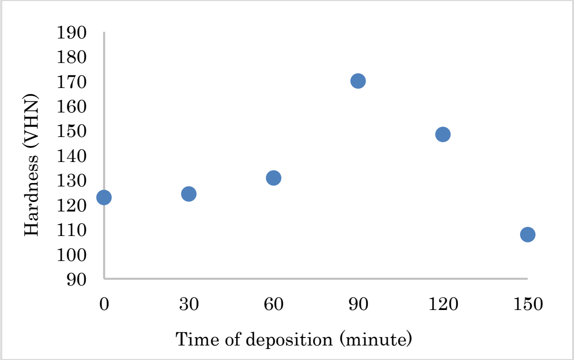


Fig. 3: Graph of hardness value of 316L stainless steel substrate and TiO_2 thin film at various deposition times.

Based on these Figure 3, it can be seen that the longer the DC-Sputtering deposition time, the higher the hardness value of the material, but only up to the point of maximum hardness at 90 minutes, then the hardness value decreases at 120 and 150 minutes. The cause of this decrease in hardness is called the passing process. saturation or re-sputtering process.In theory, the longer the deposition process, the more the number of Ti + O atoms deposited so that the material will be denser, but because the ability of the substrate atoms to dissolve Ti + O atoms is limited, thus the phenomenon of passing saturated [19].

The decrease in the hardness value is probably due to an increase in high plasma power resulting in an increase in energy and the number of Ar+ ions, so that more oxygen atoms are released when the ions collide with TiO_2 molecules. These collisions can occur on the target, the molecules towards the substrate, or on a thin layer that has been deposited. This has an impact on the destruction of the thin layer structure, so that the deposited TiO_2 thin layer becomes an amorphous structure. High plasma power causes the thin layer that has been deposited to undergo a re-sputtering process so that the film thickness is reduced [20].

3. 4.Water Contact Angle

The value of the water contact angle increased with increasing deposition time and the maximum value was obtained at 90 minutes of deposition, before finally decreasing at 120 and 150 minutes.

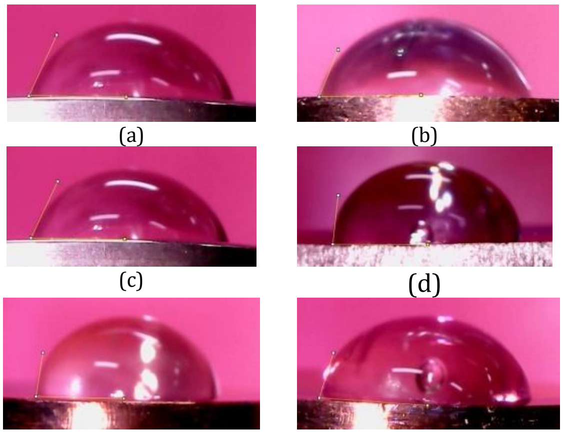

(a) (b)
(c) (d)
(e) (f)

Fig. 4: Test results of side view of water contact angle on (a) 316L stainless steel substrate and DC-Sputtering material with time variations (b) 30 minutes, (c) 60 minutes, (d) 90 minutes, (e) 120 minutes, (f) 150 minutes.

At maximum condition, TiO_2 coating can increase the water contact angle value by 22.1% from 316L stainless steel substrate. The photo of the water contact angle of the 316L stainless steel substrate and the TiO_2 thin layer at various variations in deposition time is shown in Fig. 4.

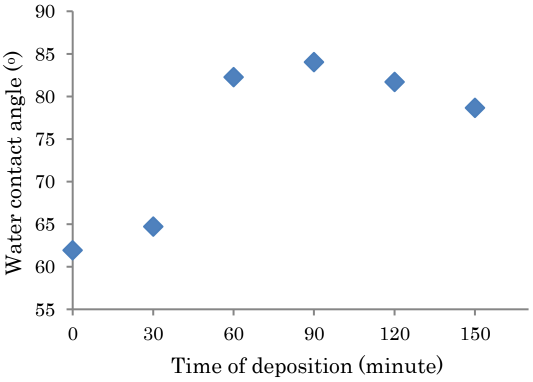


Fig. 5: Graph of the water contact angle value of 316L stainless steel substrate and TiO_2 thin film on various variations of deposition time.

Based on the water contact angle test data shown in Fig. 5, information is obtained that the structure of the TiO2 layer has hydrophilic properties [21] and has the potential to become hydrophobic if treated on materials that support these properties [22].

A material can be categorized as a hydrophilic material if it has a water contact angle in the range of 5° ~ 90° [23] and will become hydrophobic if it has a water contact angle in the range of 91° ~ 150° [24]. A contact angle of less than 90° is observed when the liquid spreads on the surface, while a contact angle of more than 90° is observed when there are small droplets of liquid on the surface. The smaller the contact angle, the higher the affinity for the liquid [25].

The increase in the value of the water contact angle indicates that the wettability on the TiO_2 surface is increasingly unproductive when it reaches the optimum point at 90 minutes of deposition, because the fluid will minimize its contact with the surface and form dense liquid droplets and the liquid will clot more. This process exhibits an increasingly hydrophobic surface. If the material is more hydrophobic, it will reduce the corrosion rate because the tendency of the material to interact with the liquid or its environment is getting less and less [26].

Drops of pure liquid on a solid surface can show adhesion forces between the liquid and the solid surface which result in the spread of the liquid or known as wettability, while the intermolecular cohesion forces tend to negate the dispersion of the liquid [27].

Adhesion forces will cause two substances to stick together when mixed or brought together, while the occurrence of cohesion forces is influenced by the density and distance between particles in an increasingly dense substance. If a polar liquid is dropped on a polar plate, a contact angle will not be formed. The contact angle can occur because of the adhesion force between the solid and the liquid and the cohesion force between the liquid molecules. The smaller the contact angle obtained, the greater the adhesion force. The greater the contact angle obtained, the greater the cohesion force [28].

4. Conclusion

In this study, it can be concluded that the TiO_2 layer on the 316L stainless steel substrate surface has been successfully deposited using the DC-Sputtering method with variations in time of 30 minutes, 60 minutes, 90 minutes, 120 minutes and 150 minutes. The TiO_2 layer has a monoclinic crystal structure in the plane (220) at a deposition time of 90 and in the plane (133) at a deposition time of 30, 60, 120 and 150 minutes, and the crystallite size range is ~7.90887 nm to ~18.94568. nm. The deposition of a thin layer of TiO_2 succeeded in increasing the hardness value of the 316L stainless steel substrate, with the highest hardness value of 170,105 VHN at a deposition time of 90 minutes. The structure of the formed TiO_2 layer has hydrophilic properties.

5. Conflict of Interest

The authors declare that they have no conflict of interest.

References

[1] I. Ferreri, V. S. Calderon, R. G. Escobar, C. Palacio, M. Henriques, A. P. Piedade, and S. Carvalho, "Silver activation on thin films of Ag-ZrCN coatings for antimicrobial activity," *Mat.Sci. and Eng. C*, **55**, 547–555, (2015).

[2] Y. Wang, S. Wang, Y. Zou, Y. Wu, G. Chen, J. Ouyang, D. Jia, and Y. Zhou, "A self-adjusting PTFE/TiO_2 hydrophobic double-layer coating for corrosion resistance and electrical insulation," *Chem. Eng. J.*, **402**, 126-136, (2020).

[3] Tavares, Mainier, F. Zimmerman, R. Freitas, and C. M. I. Ajus, "Characterization of prematurely failed stainless steel orthopedic implants," *Eng Fail Anal.,* 1246–1253, (2010).

[4] Q. Chen and G. A. Thouas, "Metallic implant biomaterials," *Mat. Sci. and Eng. R: Reports*, **87**, 1–57, (2015).

[5] A. Setiawan, and A. K. Dewi, "Zinc Phosphate Coated Carbon Steel Corrosion On Sulfuric Acid Media," *J. Teknologi*, **11**, 57–66, (2019).

[6] I. D. Cita and B. A. Kurniawan, "The Effect of Alloy Composition and Coating Thickness on the Process of Flame-Sprayed Coating Zn-Al Powder on Corrosion Rate of Carbon Steel," *Master's Program Thesis, Institut Teknologi Sepuluh Nopember*, 111-124, (2017).

[7] M. Lelis, S. Tuckute, S. Varnagiris, M. Urbonavicius, G. Laukaitis, and K. Bockute, "Tailoring of TiO_2 film microstructure by pulsed-DC and RF magnetron co-sputtering," Surf. and Coat. Tech., 377, (2019).

[8] D. A. Florea, D. Albuleț, A. M. Grumezescu, and E. Andronescu, "Surface modification – A step forward to overcome the current challenges in orthopedic industry and to obtain an improved osseointegration and antimicrobial properties," *Mat. Chem. Phys.*, **243**, 122-579, (2020).

[9] W. Bai, K. Chen, J. Chen, J. Xu, H. Lin, Y. Lin, Y. Xu, and J. Lin, "Natural Highly-hydrophobic urushiol/TiO_2 coated cotton fabric for effective oil–water separation in highly acidic alkaline and salty environment," *Separat. and Purif. Tech.*, **253**, 117-195, (2020).

[10] W. Chen, X. Ran, X. Jiang, H. Min, D. Li, L. Zou, J. Fan, and G. Li, "Synthesis of TiO_2 and TiO_2/Pt and Their Application in Photocatalytic Degradation of Humic Acid," *Wat. Env. Res.*, **86**, 48–55, (2014).

[11] A. Setyani and E. A. P. Wibowo, "Fabrication of Titanium Dioxide (TiO_2) Nanotubes Using the Hydrothermal Method," *J. Kimia VALENSI*, **3**, 20–26, (2017).

[12] T. Sujitno, A. Santoso, Wiryoadi, Sayono, B. Siswanto, and L. Susita, "Optimization of the sputtering process parameters on the deposition of a thin layer of titanium nitride (TiN) on aluminum," *Proc. of Meetings and Presentations. Penelitian Dasar IImu Pengetahuan Dan Teknologi Nuklir P3TM-BATAN*, 156–165, (2002).

[13] J. B. Bellam, G. Kandikunta, B. Manupati, S. Debabrata, P. George, and V. Verma, "DC sputter deposited TiO_2 thin film on ITO/glass substrate for perovskite based solar cell application," *Materials Today: Proceedings,*34-38, (2020).

[14] J. H. Lee, G. E. Jang, and Y. H. Jun, "Investigation and evaluation of structural color of TiO_2 coating on stainless steel, "*Ceramics International*, **38,** (SUPPL. 1), S661–S664, (2012).

[15] W. Andriyanti, "Low temperature plasma nitriding and oxidizing of CP-Titanium," *Master's Program Thesis, Institut Teknologi Bandung*, 12-51, (2016).

[16] I. Hafizi, W. Widjijono, and M. H. N. E Soesatyo, "Determination of the concentration of stainless steel 316L and cobalt chromium remanium GM-800 in the GPMT test," *Majalah Kedokteran Gigi Indonesia*, **2**, 3, 121, (2016).

[17] ASTM, "Standard Specification for Chromium and Chromium-Nickel Stainless Steel Plate, Sheet, and Strip for Pressure Vessels and for General Applications, in: A 240/A 240M," *ASTM International, United States of America*, 13-19, (2004).

[18] S. Hadiati, "Study of Annealing Temperature Variations and Holding Time on the Growth of Bazr0.15ti0.85o3 Thin Layers Using Sol Gel Method," *Jurnal MIPA*, **36**, 1, 20–27, (2013).

[19] Sulhadi, S. Wahyuni, S. Mulyani, V. A. Carieta, D. Aryanto, Sugianto, and P. Marwoto, "Fabrikasi Film Tipis ZnO; Ga Thin Film Fabrication with DC Magnetron Sputtering Method Effect of Plasma Power and Anneling Temperature," 228-233, (2019).

[20] M. D. Sulisa, “Effect of Static Contact Angle on Droplet Spread over a Heated Solid Surface at Medium Weber Numbers,” *Jurnal Mechanical,* **1**, 1-2, (2010).

[21] Y. Takata, S. Hidaka, M. Masuda, and T. Ito, “Pool Boiling on a Superhydrophilic Surface,” *I. J. Energy Res.*, **27**, 111–119, (2003).

[22] J. Suroto, “Effect of Wettability Value on Pool Boiling Heat Transfer Case Study Hydrophobic, Hydrophilic and Superhydrophilic,” *Jurnal Ilmu Dan Inovasi Fisika*, **1**, 1, 65–69, (2017).

[23] L. B. Turnip, S. Handani, and S. Mulyadi, “Effect of Addition of Mangosteen Peel Extract Inhibitor to Decrease the Corrosion Rate of ST-37 Steel,” *Jurnal Fisika Unand*, **4**, 2, 144–149, (2017).

[24] G. Lamour, A. Hamraoui, A. Buvailo, Y. Xing, S. Keuleyan, V. Prakash, A. Eftekhari-Bafrooei, and E. Borguet, “Contact Angle Measurements Using a Simplified Experimental Setup,” *J. Chem. Educ.*, **87**, 1403–1407, (2010).

[25] J. Fritzsche and U. A. Peuker, “Wetting and Adhesive Forces on Rough Surfaces – An Experimental and Theoretical Study,” *Procedia Eng., New Paradigm of Particle Science and Technology Proceedings of The 7th World Congress on Particle Technology*, **102**, 45–53, (2015).