



Surface characterization of poly(methylmethacrylate) based nanocomposite thin films containing Al₂O₃ and TiO₂ nanoparticles

S. Lewis^{a,*}, V. Haynes^a, R. Wheeler-Jones^b, J. Sly^c, R.M. Perks^b, L. Piccirillo^a

^a School of Physics and Astronomy, Radio Astronomy Technology Group, The University of Manchester, Turing Building, Oxford Rd, Manchester, M13 9PL, United Kingdom

^b The Institute of Advanced Materials and Energy Systems, Cardiff School of Engineering, Queen's Buildings, The Parade, Cardiff CF24 3AA, United Kingdom

^c School of Electrical and Electronic Engineering, Microelectronics and Nanostructures group, The University of Manchester, Sackville St Building, Sackville St, Manchester, M60 1QD, United Kingdom

ARTICLE INFO

Article history:

Received 15 April 2008

Received in revised form 24 August 2009

Accepted 4 September 2009

Available online 16 September 2009

Keywords:

Poly(MethylMethAcrylate)

Aluminum oxide

Titanium oxide

Nanoparticles

Nanocomposites

Atomic force microscopy

Electron beam resist

ABSTRACT

Poly(methylmethacrylate) (PMMA) based nanocomposite electron beam resists have been demonstrated by spin coating techniques. When TiO₂ and Al₂O₃ nanoparticles were directly dispersed into the PMMA polymer matrix, the resulting nanocomposites produced poor quality films with surface roughnesses of 322 and 402 nm respectively. To improve the surface of the resists, the oxide nanoparticles were encapsulated in toluene and methanol. Using the zeta potential parameter, it was found that the stabilities of the toluene/oxide nanoparticle suspensions were 7.7 mV and 19.4 mV respectively, meaning that the suspension was not stable. However, when the TiO₂ and Al₂O₃ nanoparticles were encapsulated in methanol the zeta potential parameter was 31.9 mV and 39.2 mV respectively. Therefore, the nanoparticle suspension was stable. This method improved the surface roughness of PMMA based nanocomposite thin films by a factor of 6.6 and 6.4, when TiO₂ and Al₂O₃ were suspended in methanol before being dispersed into the PMMA polymer.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Poly(methylmethacrylate) (PMMA) is a well-known electron beam resist. The minimum feature size that can be obtained is approximately 10 nm [1]. Unfortunately, it has a maximum aspect ratio of approximately 4:1. Therefore, to achieve features of this geometry the film thickness must be approximately 40–50 nm, in order to overcome the proximity effects. This is due to the fact that at an acceleration voltage of 25 keV the electrons elastically and inelastically scatter in arbitrary directions away from the primary trajectory whilst penetrating through the resist. To transfer these nanoscaled structures into a semiconductor like silicon (Si) or gallium arsenide (GaAs), dry etching techniques such as reactive ion etching (RIE) and inductively couple plasma (ICP) are utilized. However, the etch rate of the PMMA resist is usually much faster than the etch rate of the semiconductor because it is an organic material. Therefore, at thicknesses of 40–50 nm the PMMA resist will etch before the semiconductor. To overcome this, the PMMA resist thickness must be increased to the order of hundreds of nanometers. If the thickness of the PMMA resist is 100 nm, the effect of the scattering may give electron trajectories with a spread of up to 50 nm, causing the resultant feature to collapse. Also secondary electrons are generated and are scattered in arbitrary trajectories over 1 μm away from the

primary trajectory. This also gives rise to the collapsing of the desired feature. Therefore, 10 nm nanostructures cannot be fabricated at this thickness.

However, it has been suspected that dispersing a higher density material into the PMMA, to create a nanocomposite resist, will confine the electron spread to the primary trajectory and minimize the amount of secondary electrons being generated [2]. Therefore, the thickness of the PMMA resist can be increased to achieve a high aspect ratio. Also, the etch rate of the resist should be reduced when the nanoparticles are introduced into the PMMA [3,4].

To achieve high resolution nanostructures in the PMMA based nanocomposite resist, the first requirement is that the dispersion of the nanoparticles must be well defined. It has often proved difficult to form a stable dispersion of nanoparticles in polymer matrices, as the nanoparticles tend to aggregate. The strength of the inter-nanoparticle coupling in liquids typically ranges from weak van der Waals interactions to relatively strong hydrogen bonding. The geometrical form of the nanoparticle aggregates can be string, network, or globular structures.

The surface nature of these oxide nanoparticle species is hydrophilic due to the existence of hydroxyl groups [5]. In order to disperse the nanoparticle in a hydrophobic polymer matrix, the interfacial interaction must be improved. Modification of the nanoparticle surface with different interfacial methods has been applied. Such techniques involve the encapsulation of the nanoparticle by emulsion polymerization in PMMA [6].

* Corresponding author.

E-mail address: Scott.Lewis@Manchester.ac.uk (S. Lewis).

This investigation describes a protocol for the preparation of reasonably high concentrations of TiO₂ and Al₂O₃ nanoparticles uniformly embedded in the PMMA polymer matrix to achieve TiO₂/PMMA and Al₂O₃/PMMA nanocomposite resist.

2. Experimental details

2.1. Preparation of the PMMA based nanocomposite resist

The PMMA based nanocomposites used in this investigation were prepared by the homogeneous dispersal of 15–25 nm diameter Al₂O₃ and TiO₂ nanoparticles (obtained from MKnano.com 99.999%) in PMMA.

Samples were prepared by dissolving the PMMA (obtained from Sigma-Aldrich) in the solvent anisole (obtained from Sigma-Aldrich 97%). Anisole dissolves the PMMA by unraveling the PMMA particles into molecular chains. The molecular weight of the PMMA was 950 K and the PMMA was used 'as is'. The ratio of the PMMA to anisole was kept at 7% by dissolving 350 mg of PMMA in 4.65 g of anisole. The anisole was filtered under vacuum through a 25 nm cellulose nitride membrane filter (obtained from Millipore). The PMMA/anisole samples were shaken using an IKA rotary/gyrative shaker for 96 h, in order for the anisole to fully dissolve the PMMA. This was repeated four times.

The Al₂O₃ and TiO₂ nanoparticles were filtered through a 25 nm membrane filter, to obtain 15–25 nm nanoparticles. This was achieved by measuring the Al₂O₃ nanoparticles by weight to 550 mg. These were directly dispersed into 1 L of deionized water. The deionized water/nanoparticles were filtered under vacuum. Next, the deionized water/nanoparticle samples were put in a desiccator to absorb the deionized water leaving behind the appropriate nanoparticles. The Al₂O₃ nanoparticles were then weighed out to obtain two samples of 200 mg. The first sample was directly dispersed into PMMA/anisole and the second was dispersed into 0.5 ml of methanol (obtained from Sigma-Aldrich 99.9%) to produce a nanoparticle suspension before being mixed with the PMMA/anisole solution. The Al₂O₃ nanoparticles that were suspended in methanol were added to the PMMA/anisole solution and then shaken for 36 h to achieve a good nanoparticle suspension in the PMMA mix. This whole procedure was repeated for the TiO₂ nanoparticles.

These PMMA based nanocomposite resists were then spun onto gold (Au) coated 24 mm × 24 mm borosilicate glass cover slips. The cover slips were first sputter coated with a 7 nm layer of gold to promote adhesion of the nanocomposite resist to the borosilicate substrate. The PMMA based nanocomposite resist was spun-on using a spin cycle of 4000 rpm for 45 s, which was followed by a soft bake at 180 °C for 3 min, to allow the anisole and methanol to evaporate.

2.2. Characterization of the PMMA based nanocomposite resist surface

The overall thickness of the PMMA based nanocomposite resist films was measured using an Atomic Force Microscope (AFM) after spinning, soft baking and exposure to the electron beam. The samples were exposed on a converted SEM, JOEL JSM 840A, driven by Elphy quantum software. The samples were exposed with an acceleration voltage of 25 keV and beam current of 40 pA at a working distance of 7 mm. Development was carried out in solutions of MIBK (Methyl IsoButyl Ketone) and IPA (IsoProPanol), in the ratio of 1:3, for 30 s followed by a 40 s rinse in IPA.

The exposure clearing dose of each resist was determined from a matrix of a hundred 10 μm squares that were exposed with a dose scale in incremental steps of 30 μC/cm². The dose was increased in both directions with the square in the lower left having a dose of 30 μC/cm², and that of the upper right having a dose of 600 μC/cm². The size of the squares allowed for accurate AFM measurements of the remaining resist thickness for each dose, and hence the clearing dose could be determined of each resist. For the nanocomposite resists which the

TiO₂ and Al₂O₃ nanoparticles were directly dispersed the exposure clearing doses were 390 and 410 μC/cm² respectively whereas when the TiO₂ and Al₂O₃ nanoparticles were directly dispersed into the PMMA polymer matrix the exposure clearing doses were 300 μC/cm² respectively.

The thickness measurements were obtained using a surface probe microscope topometrix explorer in non-contact mode. The AFM tips were cantilevers operating at a frequency range of 279–313 kHz. The length of the cantilever was 134 μm, width 28 μm and the thickness was 3.7 μm. The pyramidal tip was 3 μm with a base of 10 μm high, the tip radius was <20 nm and the force applied was 25–38 Nm⁻¹. The thickness was found to be dependent on the dispersal method. When the TiO₂ and Al₂O₃ nanoparticles were directly dispersed into the PMMA polymer matrix the resultant thicknesses were 736 and 803 nm, respectively. However, the thicknesses of the PMMA based nanocomposite resist were 609 and 627 nm when the TiO₂ and Al₂O₃ nanoparticles were suspended in methanol before dispersed into PMMA polymer matrix respectively. To determine the surface roughness of all the samples, the average was taken of the peaks and troughs, measured in 10 μm squares.

2.3. Characterization of dispersion mechanisms and the oxide nanoparticle surface properties

The stability of the oxide nanoparticle dispersion in the PMMA/anisole can be determined by understanding the behaviour of the bonding mechanism between the various solvents used to disperse the oxide nanoparticles. This will identify which solvents are most appropriate for this task. The solvents considered initially were toluene, xylene, anisole, isopropanol (IPA), methanol, acetic acid (all obtained from Sigma-Aldrich) and deionized water. It should be noted that acetone was not used, because, the PMMA molecule breaks down in acetone (acetone is used the strip PMMA from the substrate).

The interaction between the surface of the oxide nanoparticles and the encapsulating solvents will determine the effectiveness of the dispersion of the oxide nanoparticles in the solvents. This interaction can be predicted by means of contact angle measurements and a suitable hydrophilic surface.

In this experiment, the oxide nanoparticle surface was substituted by borosilicate glass; this was done because the oxide nanoparticles are too small to characterize their performance directly using conventional contact angle measurements. To increase the hydrophilic surface state of the borosilicate glass (as this will give more of a surface contact contrast when the various solvents are dropped on to it), it was prepared using ammonia hydroxide (Sigma-Aldrich) NH₄OH, hydrogen peroxide H₂O₂ (Sigma-Aldrich) and deionized H₂O solution in a ratio of 1:1:5. The hydrophilic solution was then brought to its boiling point and the borosilicate glass placed in it for 15 min. This produced a hydrophilic surface state on the borosilicate glass. The various solvents (stated above) were dropped on to the borosilicate glass using a pipette. The contact angle was then measured using a microscope.

2.4. Characterization of the stability of the oxide nanoparticle dispersion

In order to quantify the stability of the nanoparticle dispersion, 200 mg of nanoparticles was dispersed in 0.5 ml of solvent, respectively. The nanoparticle stability was assessed by a zeta potential measurement. This was performed using a Malvern ZS zeta sizer nanoseries which incorporated a laser Doppler velocimeter in combination with phase analysis light scattering technique called "M3-PALS".

3. Results and discussion

The AFM images in Fig. 1a, b show that the surface of the nanocomposite film (loaded with 200 mg of oxide nanoparticle) was not homogeneous when the oxide nanoparticles were directly dispersed

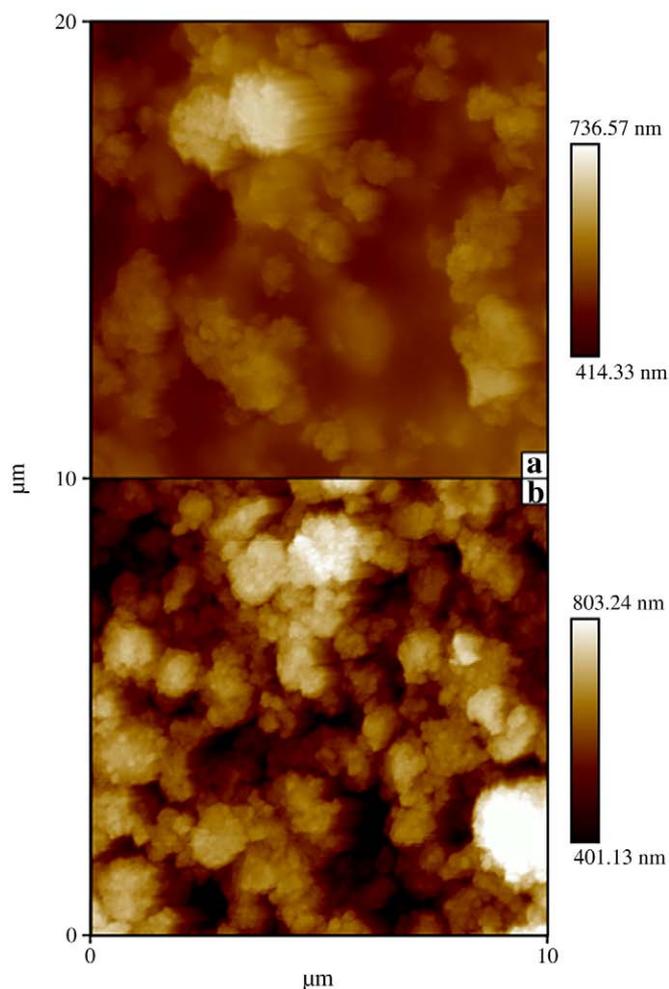


Fig. 1. AFM images of the surface of the PMMA based nanocomposite thin film in which a) TiO₂ and b) Al₂O₃ nanoparticles are embedded directly into the PMMA matrix without pretreatment in methanol.

into the PMMA polymer matrix; the rms (root mean square) roughness of the TiO₂/PMMA and Al₂O₃/PMMA nanocomposite surfaces were of 322 and 402 nm respectively.

Both oxide nanoparticle species were suspected to unbalance the depletion effects and osmotic pressures in the PMMA where the 'depletion' of polymer molecules from the region between closely spaced nanoparticles leads to an effective inter-nanoparticle attraction. The mechanism behind this is that each nanoparticle is surrounded by a depletion zone; this is the region immediately next to each nanoparticle surface. When the nanoparticles are introduced into the PMMA/anisole, the unbalanced osmotic pressure pushes the nanoparticles towards one another. Hence, nanoparticle aggregation occurs when the depletion regions of two nanoparticles intersect.

To improve the surface of the PMMA based nanocomposite resist, the nanoparticle surface must be encapsulated, so that they will repel each other and be homogeneously dispersed in the PMMA/anisole. Therefore, the nanoparticles must be suspended in a solvent first. It is this property that governs the resist's viscosity and so its overall thickness. As the quantity of solvent is increased, the PMMA polymer thickness decreases, as it becomes less viscous. As discussed above, the choice of solvent is critical.

Fig. 2 shows the contact angle of each solvent that was dropped onto the surface of the borosilicate glass. It can be seen that the solvents that have polarity indexes of less than four (toluene, xylene and anisole), had larger contact angles, suggesting that the solvents are repelled from the borosilicate glass as their molecules do not

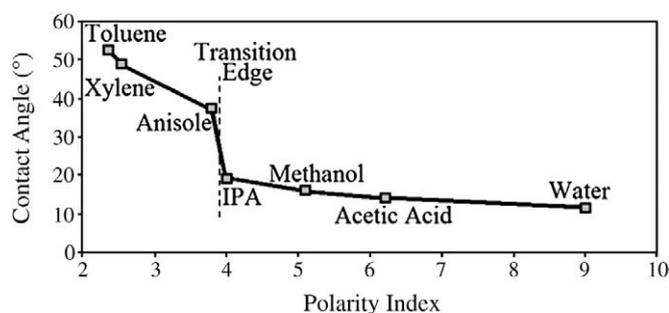


Fig. 2. Contact angles of the solvents on borosilicate glass.

incorporate any OH groups and hydrogen bonding cannot take place. The solvents with a polarity index more than four had a smaller contact angle, suggesting an attraction between the solvents and the borosilicate glass. This was due to the fact that OH groups are attached to the molecule. Hence, hydrogen bonding can take place.

Hydrogen bonding between the solvent (polarity index higher than 4.0) and the oxide nanoparticles will stabilize the oxide nanoparticle suspension. The data from Fig. 2 suggest that the toluene, xylene and anisole will not uniformly suspend the oxide nanoparticles because there is no mechanism for hydrogen bonding process to occur. This is because the dipoles within the hydroxyl groups are not present. There is no barrier immediate to the surface of the oxide nanoparticle. This allows the depletion region around each oxide nanoparticle to intersect and therefore, the oxide nanoparticles are attracted to one another, hence, aggregation. As the PMMA polymer is dissolved in anisole, it is not surprising that when the oxide nanoparticles were dispersed directly into the PMMA/anisole system, they were not suspended homogeneously.

Aggregation of the oxide nanoparticles should be greatly reduced by using IPA, methanol, acetic acid or water. These molecules have hydroxyl groups within them and are attracted to the hydroxyl groups at the surface of the oxide nanoparticles via their dipoles. Therefore, they surround the oxide nanoparticle and form a physical barrier with a thickness greater than that of the depletion region which would surround the oxide nanoparticle. The depletion regions of the oxide nanoparticles can never intersect. Hence, the oxide nanoparticle attraction is greatly reduced and the oxide nanoparticle suspension is stable.

Based on the results shown in Fig. 2, methanol and toluene (contact angles of 18° and 52°, respectively) were chosen to suspend the 200 mg of oxide nanoparticles. IPA was not used because it was too close to the hydrophilic transition edge (see Fig. 2). To quantify the stability of the oxide nanoparticle suspension, the performance of the suspension was measured using the zeta potential measurement system. As discussed above, methanol and toluene should produce contrasting results.

Fig. 3 shows that methanol should suspend the oxide nanoparticles. The zeta potential values were 31.9 mV and 39.2 mV with TiO₂ and Al₂O₃ respectively. From the data here, it can be seen that the nanoparticles suspended in methanol have a zeta potential above the 30 mV threshold [7], therefore the nanoparticle suspension was stable. However, when both nanoparticle species were suspended in toluene, the zeta potential values were 7.7 mV and 19.4 mV with TiO₂ and Al₂O₃, respectively. These were below the zeta potential threshold, hence suspension instability.

As predicted, it was observed that methanol was effective to suspend the oxide nanoparticles, prior to dispersal within the PMMA polymer matrix. It was found that 200 mg of nanoparticles dispersed in 0.5 ml of toluene aggregated together and dropped out of suspension under the force of gravity, on average in less than 1 min, whereas the methanol suspended the same amount of nanoparticles for many days.

The oxide nanoparticles suspended in methanol could be dispersed in the PMMA/anisole system. This improved the homogeneity of the surface, as shown by the AFM images in Fig. 4. Fig. 4a shows the PMMA

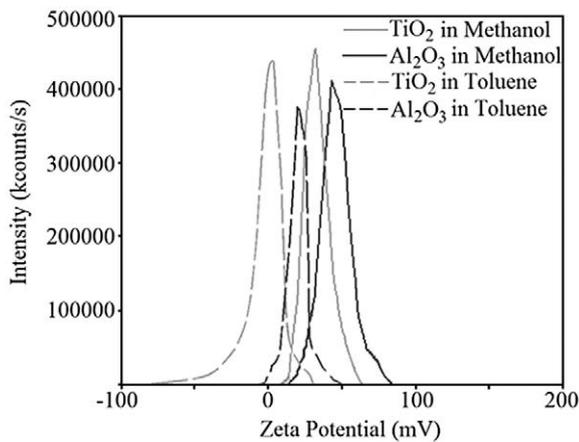


Fig. 3. Zeta potential of the oxide nanoparticles suspended in methanol and toluene respectively.

based nanocomposite thin film (after it was spun and soft baked) that was produced when the TiO_2 nanoparticles were treated with 0.5 ml of methanol and suspended directly in the PMMA polymer matrix/anisole system. The rms surface roughness was 49 nm. Comparing this with Fig. 4b, the rms surface roughness of the PMMA based nanocomposite thin film that contained the Al_2O_3 nanoparticles suspended in methanol

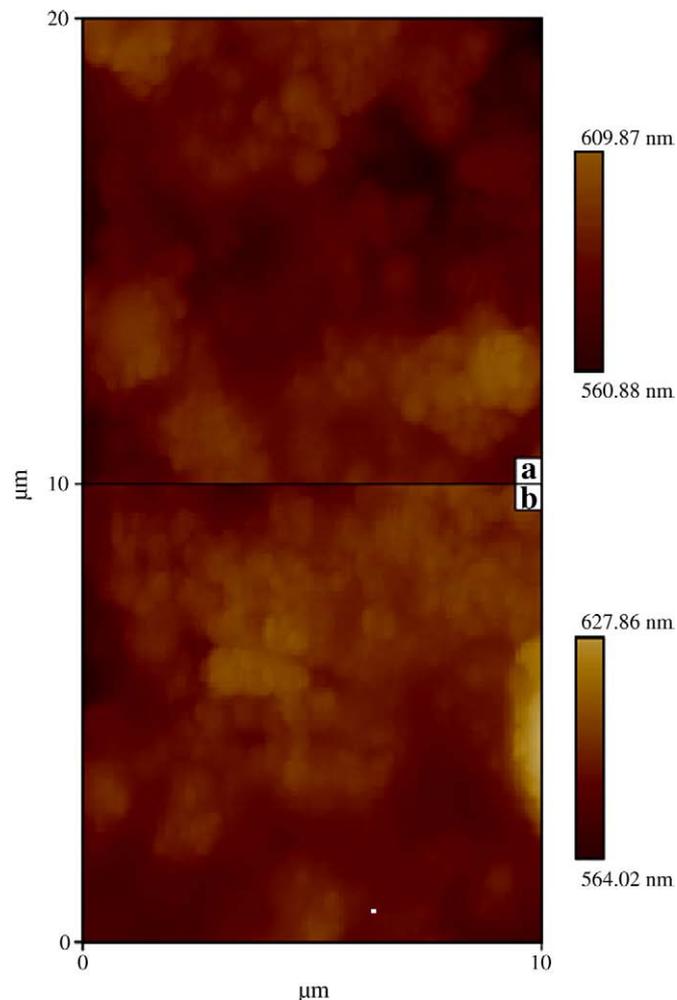


Fig. 4. AFM images of the surface of the PMMA based nanocomposite thin film in which a) TiO_2 and b) Al_2O_3 nanoparticles are embedded in the PMMA matrix after having been suspended in methanol.

was 63 nm. It must be noted that Al_2O_3 is less dense (4000 kg m^{-3}) than TiO_2 (4230 kg m^{-3}) so more Al_2O_3 nanoparticles, for a given weight can be embedded in the PMMA polymer matrix. Thus, as more nanoparticles are embedded in the PMMA polymer matrix, then the surface roughness is increased. In both cases the surface of the PMMA based nanocomposite thin films has been improved by a factor of between 6.4 and 6.6.

Fig. 5 shows the relationship between the rms surface roughness and the amount of solvent (methanol) used to suspend the nanoparticles. The surface roughness can be seen to decrease as the solvent concentration (with the oxide nanoparticles suspended within) was increased.

However, when the solvent concentration exceeded the value at x , (which for this case was 0.5 ml of methanol suspending 200 mg of oxide nanoparticles in 1.6 g of PMMA polymer/anisole), the PMMA polymer would not polymerize when baked (i.e. could not be cured). The polymer chains would not form because the increased solvent-polymer interaction caused the osmotic pressure to increase non-linearly, allowing the polymer chains to relax toward their ideal state [8]. Therefore, the polymerization (curing) cannot take place. Decreasing the volume of methanol below 0.5 ml ensures that the resist can be cured, but dramatically increases surface roughness. The optimum methanol concentration is 0.5 ml per 1.6 g PMMA/anisole.

4. Conclusion

Fabrication of a PMMA based nanocomposite electron beam resist has been demonstrated. This was achieved first by the introduction of TiO_2 and Al_2O_3 nanoparticles directly dispersed into PMMA/anisole. However, adding the oxide nanoparticles directly into the PMMA/anisole caused the nanocomposite resist surface to become inhomogeneous. This was indicated by a large value of surface rms roughness. This was found to be 322 nm and 402 nm for TiO_2 and Al_2O_3 nanoparticles respectively. This was due to poor nanoparticle dispersion as a result of the inter-nanoparticle attraction, caused by the depletion effect. Therefore, to improve the nanocomposite resist surface, the oxide nanoparticles were suspended in solvents. The anticipated effects were measured by using the zeta potential parameter. It was found that methanol suspended the oxide nanoparticles, due to the hydrogen bonding between the methanol and the oxide nanoparticles. The zeta potentials were 31.9 mV and 39.2 mV for TiO_2 and Al_2O_3 , respectively, and the oxide nanoparticle suspension was stable. However, the zeta potential value was 7.7 mV and 19.4 mV when the oxide nanoparticles were suspended in toluene and the suspension was not stable.

This method reduced the surface roughness of PMMA when TiO_2 and Al_2O_3 were suspended in methanol. The PMMA with TiO_2 nanoparticles embedded within the PMMA had an rms roughness of 49 nm and PMMA with Al_2O_3 embedded within it had an rms roughness of 63 nm. It was also found that as the solvent concentration increases, the surface

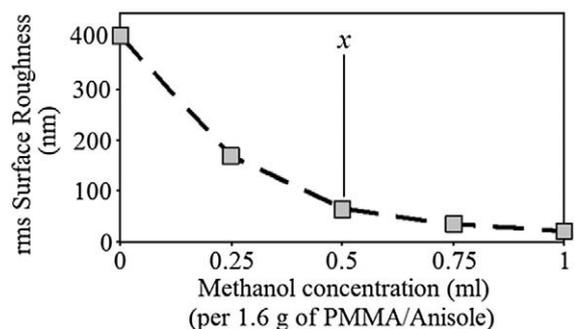


Fig. 5. Surface roughness of nanocomposite resist containing 200 mg of TiO_2 nanoparticles suspended in different volumes of methanol.

quality increased. However, there is a limit; if too much solvent was used then the PMMA would not polymerize, so could not be cured.

Acknowledgements

The authors would like acknowledge the support of C. Royston and the team at E M Systems Support Ltd and D I Westwood and H Simmonds of School of Physics and Astronomy, Cardiff University, United Kingdom, D. Jeanmaire and D. Shakeshaft of School of Physics and Astronomy, Radio Astronomy Technology Group, the University of Manchester, United Kingdom.

References

- [1] A.C.F. Hoole, M.E. Welland, A.N. Broers, *Semicond. Sci. Technol.* 12 (1997) 1166.
- [2] Y. Hu, H. Wu, K. Gonsalves, L. Merhari, *Micro. Eng* 56 (2001) 289.
- [3] L. Merhari, K.E. Gonsalves, Y. Hu, W. He, W.-S. Huang, M. Angelopoulos, W.H. Bruenger, C. Dzionk, M. Torkler, *Micro. Eng* 63 (2002) 391.
- [4] M.A. Ali, K.E. Gonsalves, A. Agrawal, A. Jeyakumar, C.L. Henderson, *Micro. Eng* 70 (2003) 19.
- [5] A. Sidorenko, S. Minko, G. Gafjichuk, S. Voronov, *Macromolecules* 32 (1999) 4530.
- [6] B. Erdem, E.D. Sudol, V.L. Dimonie, M.S. El-Aasser, *J. Polym. Sci. Part. A: Polym. Chem.* 38 (2000) 4431.