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Effect of Sputter Coating on the Observation of Polymeric Membrane Structure

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Abstract — In the present work, the effect of sputter coating, a step for preparing SEM specimen, on the observation of polymeric membrane structure was investigated by using AFM to examine the difference in membrane structure before and after sputter coating. It was observed that the sputtering process can produce coatings made up of distinguished particles. The size of the particles is on the same order of that of nodules (20 nm), which are believed by many as a basic structure of polymeric membranes. Hence, the sputter coating could affect the judgement if nodules exist in a system and influence the determination of the size of nodules. In addition, it was found that, for three PMMA membranes studied in this work, the surface is not uniform but consists of a lot of protrusions, which is believed to be aggregations of polymer (nodules). For membrane surfaces with small crevices among protrusions, it seems that the protrusions receive more coatings than the crevices during coating process, resulting in larger surface protrusions after sputter coating. On the other hand, for membrane surfaces with large crevices among protrusions, the crevices would be filled with the coating material, resulting in smaller crevices after sputter coating. The results indicate that one should be careful in using SEM to investigate the fine polymeric structure such as nodules because the coating process could influence the fine structure.

Key Words: Polymeric Membrane Structure, Sputter Coating, SEM, AFM, Nodule

INTRODUCTION

It is well known that the permeability properties of polymeric membranes are strongly related to their structure (Pusch and Walch, 1982). The most widely used technique to characterize the structure of polymeric membranes is the scanning electron microscopy (SEM). However, for observing the structure of polymeric membranes by SEM, it is required to coat the specimen surface with a very thin conductive layer to resolve the problem of specimen charging (Lawes, 1987). Sputtering is an efficient coating technique to deposit conductive material, such as gold/palladium alloy, on the surface of polymeric membranes. Theoretically, the coating layer should be as thin as possible. But, if the coating thickness is too thin it will be ineffective in eliminating the charge. For general observation on polymeric membranes, the coating layer is about 25 nm thick (Goldstein et al., 1981). Sometimes, for heat-sensitive material or under operation of high beam energy (for high resolution), thicker film might be needed to protect the specimen from thermal damage (or beam damage). Nevertheless, the deposition of a film might also cause some artifacts on the observation of membrane structure (Lawes, 1987; Goldstein et al., 1981; Kanig, 1987).

To evaluate the effect of sputter coating on the observation of polymeric membrane structure, in the present work, we used atomic force microscopy (AFM) to examine the membrane surface structure before and after metal sputtering. In AFM, the repulsive force between the tip, located at the end of a

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cantilever, and the specimen is measured, and the spatial variation of the tip-specimen repulsive force or that of the tip height is converted into an image to show the surface morphology (Magonov and Whangbo, 1996). By using AFM, the coating process is not needed and better resolution of three-dimensional surface image can be obtained. Therefore, reports of using AFM to characterize membrane structure are now increasing (Fritzsche et al., 1992, 1993; Bowen et al., 1996; Suzuki et al., 1996; Khulbe et al., 1996, 1997). Generally speaking, fine morphological variations are better detected by AFM; however, in the characterization of rough surfaces, SEM is more reliable because the imaging of steep surface might cause image artifacts in AFM analysis (Magonov and Whangbo, 1996). In this work, we used AFM to characterize the membrane surface structure before and after coating to evaluate the effect of metal sputtering.

In the present work, three poly (methyl methacrylate) (PMMA) membranes were prepared of which the gas separation performances are different. Since the separation performances are different, the structure of the three membranes could be different. As will be shown later, the AFM analysis supports that the surface structures of the three PMMA membranes are indeed different. However, on basis of the micrographs obtained by SEM, no detectable difference among them can be observed. The data presented in this work indicates that the layer resulted from sputter coating would obscure the real membrane structure and therefore no detectable difference can be observed by SEM.

Another important point discussed in this work is the effect of sputter coating on the observation of "nodular structure" in polymeric membranes. It is believed by many (Schultz and Asunmaa, 1970; Panar et al., 1973; Kamide, 1990; Kesting, 1990) that, during membrane formation, polymer chains tend to aggregate together and form nodules, which contain several tens of aggregated macromolecules and are about 200 Å in diameter. The existence of nodules can provide an explanation (Kesting and Fritzsche, 1993) for the origin of dual mode sorption (Vieth et al., 1976) and permeation (Paul and Koros, 1976) in gas separation. Hence, investigation of nodular structure in polymeric membranes would be of great help to understand the relationship between membrane structure and separation performance. However, when using SEM to study the nodular structure, the following problem should be carefully evaluated. It is known that, during sputter coating, if the cohesive forces of the deposited metal are greater than the forces between the metal and the specimen (polymer), agglomeration of the deposited metal could occur as a result of uneven deposition (Magonov and Whangbo, 1996). The uneven deposition would produce a coating layer made up of distinguishable particulate structure, the so-called "decoration artifact." (Lawes, 1987; Magonov and Whangbo, 1996). Therefore, if the size of the deposited particles is also on the same order of that of nodules, SEM analysis on such a deposited sample might not be able to reveal the real nodular structure. We will compare the membrane surface structure before and after coating to study the effect of sputtering on the observation of nodular structure.

EXPERIMENTAL

Materials

PMMA used in this study was supplied by Aldrich Chemical Co. The number averaged molecular weight is 140000 g/mol, measured by GPC. The nonsolvents and solvents were of reagent grade and used without further purification. Distilled water was used throughout this study.

Membrane preparation

PMMA was dissolved in proper solvents to form 12.5 vol % casting solutions at room temperature. The solution was cast on a glass plate to a predetermined thickness of 300 μm with a Gardner knife, and then immersed into a coagulation bath. After precipitation, the membranes were peeled off and dried in air. Three solvent/coagulant pairs were used to prepare asymmetric membranes with different structures. They were acetone/water, acetone/n-hexane, diethylene-glyco-dimethyl-ether (DGDE)/water.

SEM analysis

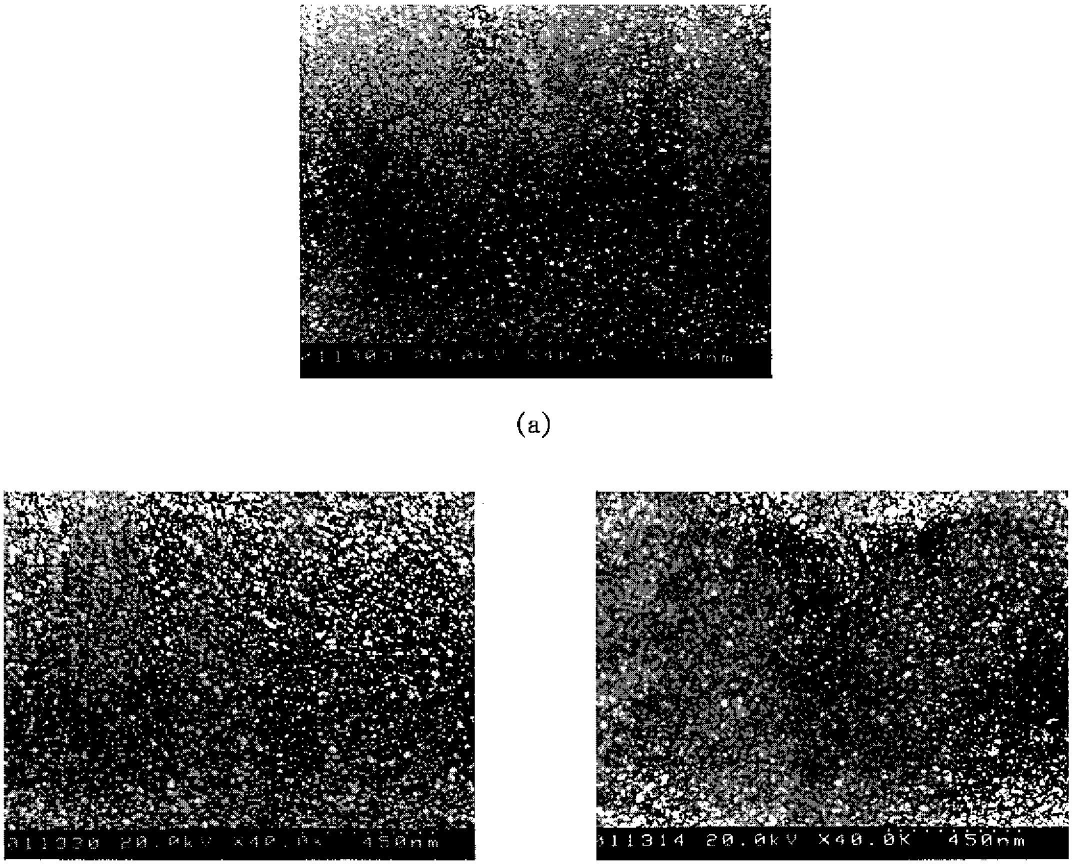
The membrane structures were examined by a Hitachi (Model S570) scanning electron microscope (SEM). In SEM studies, membrane samples were fractured in liquid nitrogen and sputter coated (Hitachi E-1030, Ion Sputter) with platinum.

AFM analysis

The membrane surface structure was examined by an atomic force microscope (Digital Instrument, DI 5000) in the tapping mode. Structures of membrane samples before and after metal sputtering were examined to determine the effect of metal sputtering on the membrane structure.

Gas flux measurement

Oxygen and nitrogen gas fluxes were determined by using the Yanaco GTR-10 gas permeation analyzer. For more detail description of the experimental



(a)

(b) (c)

Fig. 1. Scanning electron micrographs (x 40K) of the surface of the PMMA membranes prepared by different solvent/coagulant pairs. (a) DGDE/water; (b) acetone/n-hexane; (c) acetone/water.

procedure, one can refer to the work of Lai et al. (1993).

RESULTS AND DISCUSSION

Membrane surface structures before and after sputter coating

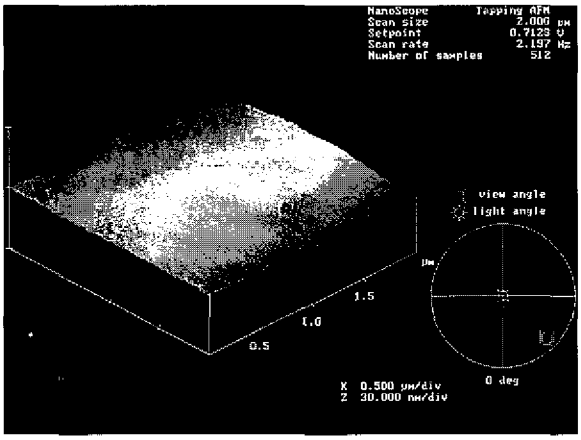
The three PMMA membranes, prepared by using acetone/water, acetone/n-hexane, DGDE/water as solvents and coagulants, possess different gas separation performance as shown in Table 1. The membrane prepared by PMMA/DGDE/water system has the highest flux and O_2/N_2 selectivity. Another system, PMMA/acetone/water, fabricates membranes possessing the lowest flux and O_2/N_2 selectivity. And the membrane prepared by the other system, PMMA/acetone/n-hexane, has flux and selectivity in between. It should be noted that the gas flux and the selectivity for membranes usually possess opposite trends; that is, higher gas flux is usually accompanied with lower selectivity. However, for the three systems studied in this work, this general trend is not followed. This observation is very interesting, and the explanation for this unusual phenomenon will be given in a subsequent paper. In this work, we are concentrating on discussing how the sputtering procedure affects the observation of the surface structures of these three membranes.

Table 1. Gas separation performance of PMMA membranes.

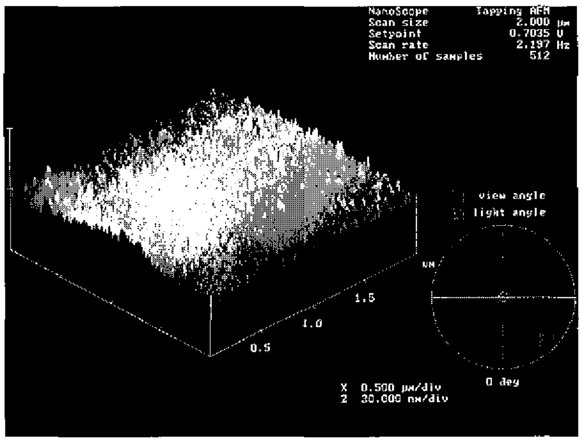
Membrane	GPU(O_2)	Selectivity (O_2/N_2)
PMMA/DGDE/water	0.19	6.44
PMMA/acetone/n-hexane	0.16	5.49
PMMA/acetone/water	0.03	2.15

* GPU = 1×10^{-6} cm^3(STP)/cm^2-sec-cmHg

It is widely accepted that the gas separation properties of membranes are strongly related to their structure (Kesting and Fritzsche, 1993). Therefore, it is reasonable to expect that the membrane structures of the above three PMMA membranes would be

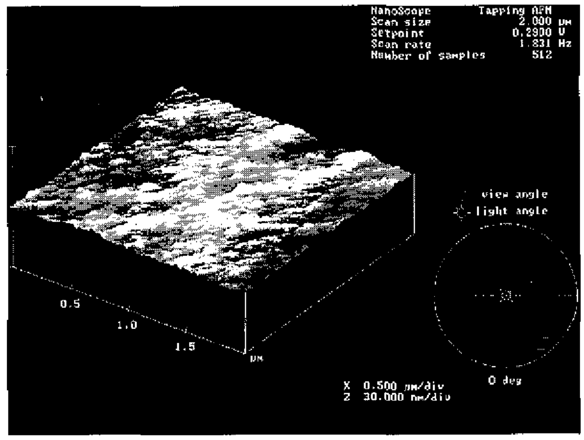


(a)

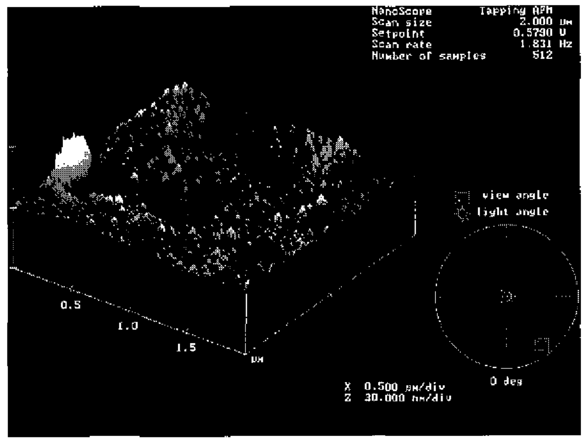


(b)

Fig.2. 3D-AFM of the surface of the membranes prepared by PMMA/DGDE/water. (a) before coating; (b) after coating 6 minutes.



(a)



(b)

Fig.3. 3D-AFM of the surface of the membranes prepared by PMMA/acetone/n-hexane. (a) before coating; (b) after coating 6 minutes.

different. However, on basis of the micrographs obtained by SEM (Fig. 1), no detectable difference among them can be observed. There are two possible reasons for the above observation. First, the difference in the membrane structure is on a finer scale, which cannot be detected by the resolution in Fig. 1; that is, magnification higher than 40,000 is required to make the difference visible. Second, the coating layer resulted from sputtering obscures the real membrane structure. As will be shown in the following, the coating layer resulted from sputter coating is responsible for why no obvious difference can be observed in Fig. 1.

Atomic force microscopy (AFM) was used to examine the membrane surface structure before and after coating to evaluate the effect of sputtering on the observation of membrane structure. The membrane surface structures of the three PMMA membranes before sputtering are presented in Figs. 2a, 3a, 4a, and those after sputtering are in Figs. 2b, 3b, 4b. Before coating, it can be seen easily that the membrane surface structures of the three membranes are different (Figs. 2a, 3a, 4a), which could account for the difference in the separation performance presented in Table I. However, after coating, the difference in the membrane surface structure is less obvious (see Figs. 2b, 3b, 4b). Figures 2-4 are the three-dimensional (3D) AFM images. Another method to present the surface structure is the two-dimensional (2D) images shown in Figs. 5 and 6, which use the degree of brightness (or darkness) to represent the variation of surface height. Figures 5 and 6 are in fact the projections of Figs 2 and 4, respectively. The 2D image of the surface structure of the membrane prepared by PMMA/acetone/n-hexane is similar to that of PMMA/DGDE/water (Fig. 5), and is hence not presented. On basis of Figs. 2-6, it can be seen very clearly that the coating process has altered the surface structure.

The above information suggests that the sputtering-coated surface could be different from the real membrane surface. Since the surface structures ob-

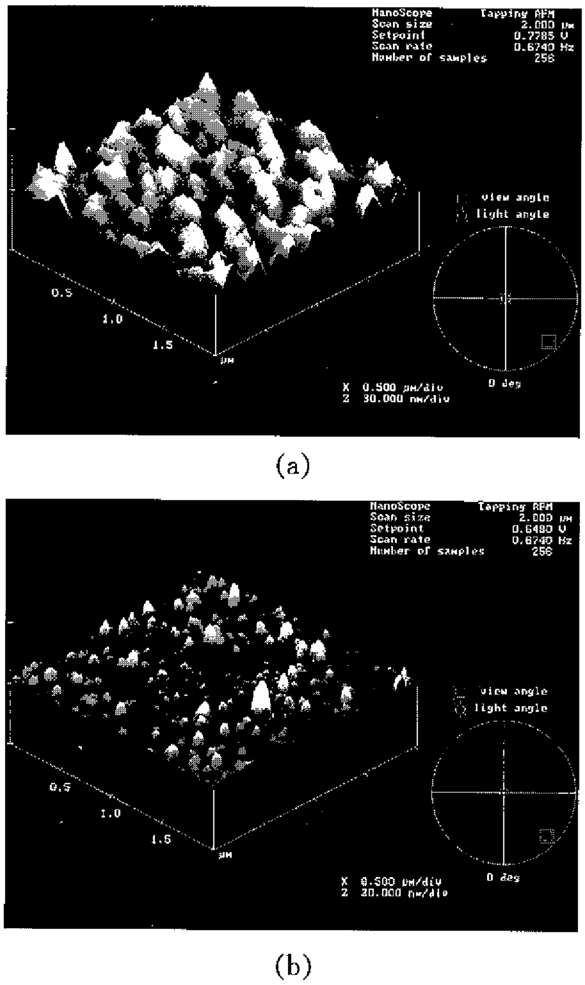


Fig.4. 3D-AFM of the surface of the membranes prepared by PMMA/acetone/water. (a) before coating; (b) after coating 6 minutes.

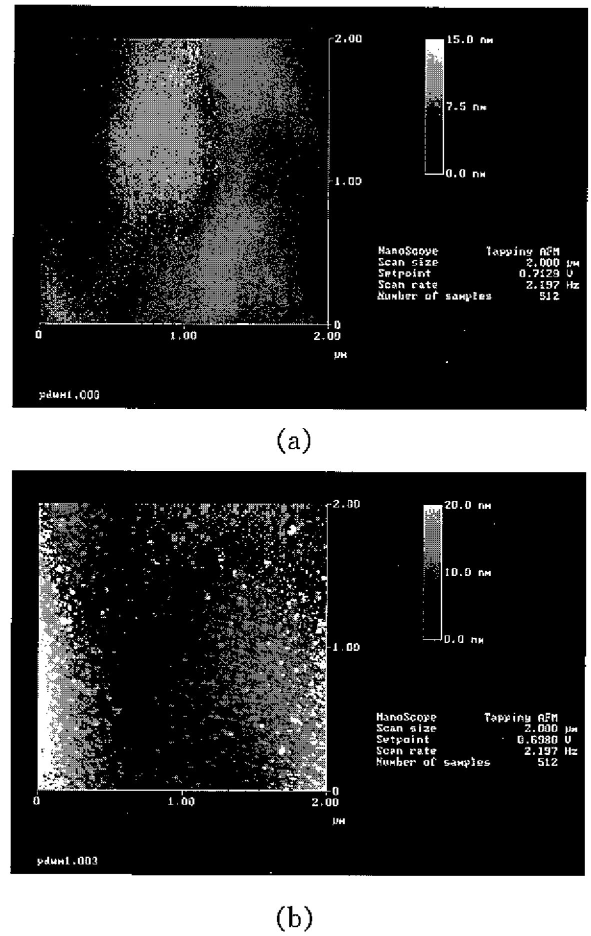


Fig.5. 2D-AFM of the surface of the membranes prepared by PMMA/DGDE/water. (a) before coating; (b) after coating 6 minutes.

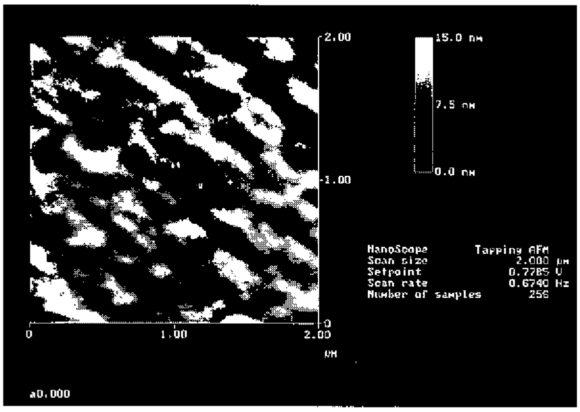
served by SEM are the coated surface but not the real surface, the SEM analysis might sometimes not be able to reveal the real membrane structure.

Effect of sputter coating on the observation of "nodular structure"

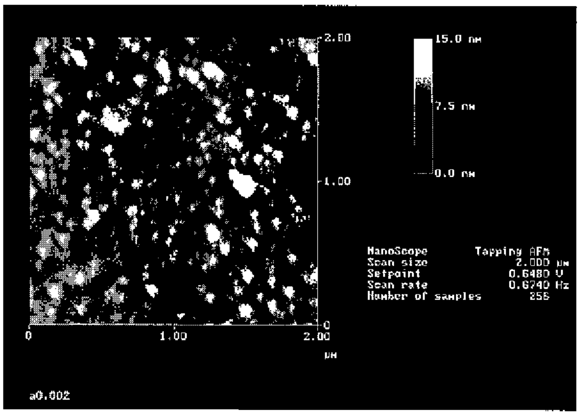
Figure 7 presents the scanning electronic micrographs of a gold foil, before and after sputter coating. It can be seen that, before coating, the metal surface is quite uniform. However, after coating, particles, about 20 nm in diameter, can be observed, suggesting that the particulate structure shown in Fig. 7b is not the original structure of the gold foil but an artifact stemming from sputter coating. By using AFM, the effect of sputter coating on the surface of the gold foil can be investigated more clearly. The AFM images of the surfaces of the gold foil before and after sputter coating are presented in Fig.8 (3D) and Fig. 9 (2D). It can be seen that the surface before coating is quite smooth and no particulate structure is observed. However, after sputter coating, a particulate surface structure occurs. Obviously, the particulate structure is not the original structure of the gold foil, but is a layer formed by uneven deposition during coating. We believe that the uneven deposition is originated from the agglomeration of the deposited material, a result when the cohesive force of the deposited metal is greater than the force between the deposited metal and the specimen (polymer) (Lawes, 1987; Magonov and Whangbo, 1996).

The above discussion suggests that the uneven deposition, originated from the agglomeration of the deposited material, could produce coatings made up of distinguishable particles. The size of the agglomerated metal can be estimated from Fig.9 to be about 15-20 nm, similar to the size estimated from SEM (Fig.7). Therefore, the membrane structure on the scale of 20 nm will be obscured by the process of sputter coating. Unfortunately, a basic structure of polymeric membranes, nodules, is on this scale.

It is believed (Kesting, 1990) by many that the basic structure of membranes is not homogeneous but



(a)



(b)

Fig.6. 2D-AFM of the surface of the membranes prepared by PMMA/acetone/water. (a) before coating; (b) after coating 6 minutes.

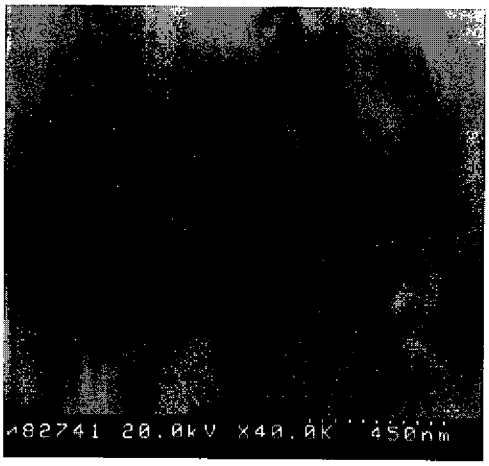
consists of small particles (aggregation of polymer chains) with a size of 200 Å (20 nm), the so-called nodules. The SEM's shown in Fig.1 indicate that the membrane structure is not uniform but consists of distinguishable particles, supporting the assertion of the existence of nodules. However, as discussed in the preceding paragraph, the size of the agglomerated metal generated from sputter coating is on the order of 20 nm, similar to the size of nodules. Therefore, it is difficult to tell if the particulate structure in SEM (Fig.1) is the real membrane structure or just an artifact from sputter coating. To clear this point, direct observation on the membranes without coating is required. It can be easily seen from Figs. 4a that the membrane surface (before coating) for the system of PMMA/acetone/water is not homogeneous, which can be told from the variation of surface height. The scales in Figs. 2a and 3a are not fine enough to show the surface height variation for the other two membrane formation systems: PMMA/acetone/n-hexane and PMMA/DGDE /water. Figures with finer scales are presented in Fig. 10, showing that the membrane surface is not uniform but consists of a lot of protrusions on the surface. The above experimental evidence supports the assertion of the existence of nodules.

On basis of Figs. 5a and 10a, it can be estimated that the dimension of the surface protrusions on the horizontal direction is about 20 nm, roughly the scale of nodules. However, the height of the protrusions is only about 2 nm, much less than the proposed size of nodules. This could be explained by the flattening effect due to the interfacial tension on the membrane surface during membrane formation (Panar et al., 1973; Kesting, 1990). On the other hand, for the system of PMMA/acetone/water (Fig. 4a), the vertical size of the surface protrusions is about 10 nm, and the horizontal size is about 200 nm. The size of these protrusions is much larger than the size of nodules; therefore, they should not be nodules. By carefully examine the surface structure shown in Fig. 6a, it can be seen (although not very clear) that the large protrusions are composed of small particles with a size of about 30 nm, similar to the size of nodules. Therefore, we believe the large surface protrusions shown in Fig. 4a are the aggregates of nodules (Kesting, 1990).

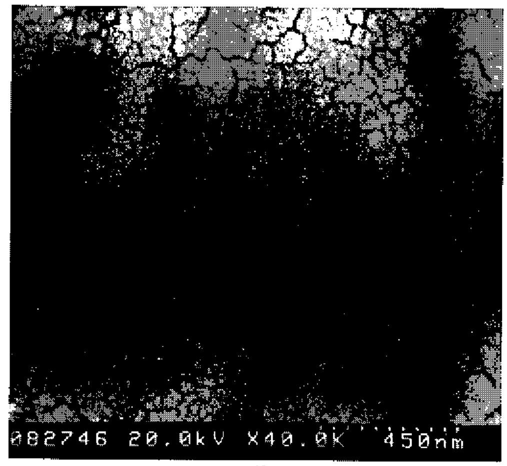
Since the size of the metal agglomerations are on the same order of the size of nodules, the sputter coating process is expected to have dramatic effect on the observation of the nodular structure in polymeric membranes. This effect can be evaluated by comparing the size of the surface protrusions before and after coating (compare Figs. 2a-6a with Figs, 2b-6b). It can be seen that , after coating, the nodular structure becomes much more prominent and the size of the nodules (surface protrusions) has also been altered. On the basis of above discussion, it can be concluded that the sputter coating can generate particles of agglomerated metal, which can affect the judgement on if nodules exist in a system (such as the case of gold foil) or influence the determination of the size of nodules (such as the case of PMMA membranes).

Effect of sputter coating on the observation of membrane surface structure

It is now known that, during sputter coating, the coating layer is not uniform but consists of particles of agglomerated metal. The size of the particles is on the same order as that of nodules, and the observation of nodules is therefore strongly affected by the coating process. In the following, we will discuss how the coating process affects the membrane surface structure. According to Figs. 2-4, it can be seen that the membrane surface (before sputter coating) is not uniform but consists of distinguishable particle structure (protrusions on the surface), which is believed to be aggregation of polymers. Before sputter coating,

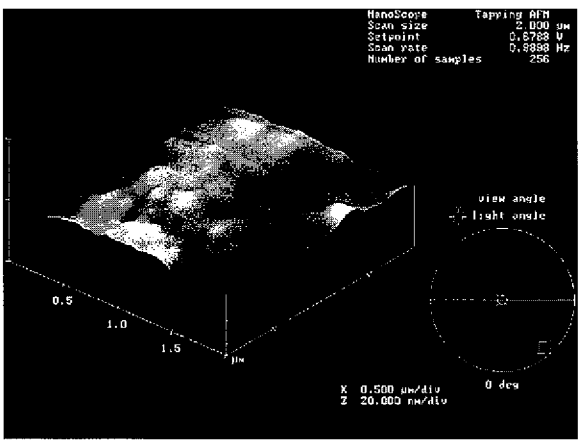


(a)

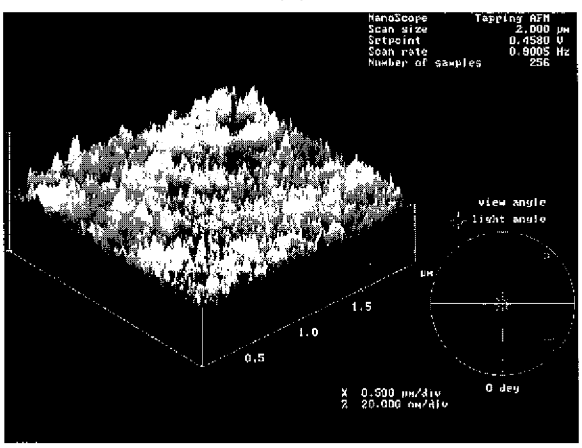


(b)

Fig. 7. Scanning electron micrographs of the surface of a gold foil. (a) before coating; (b) after coating 6 minutes.

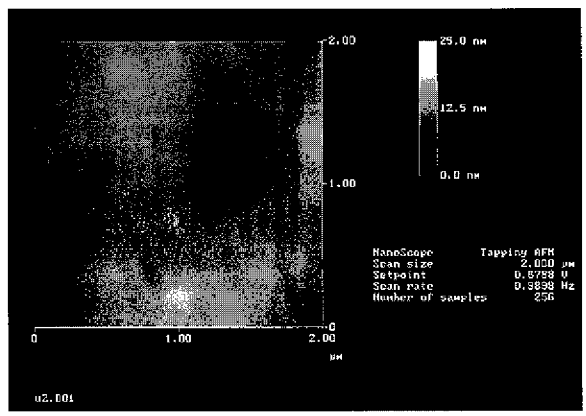


(a)

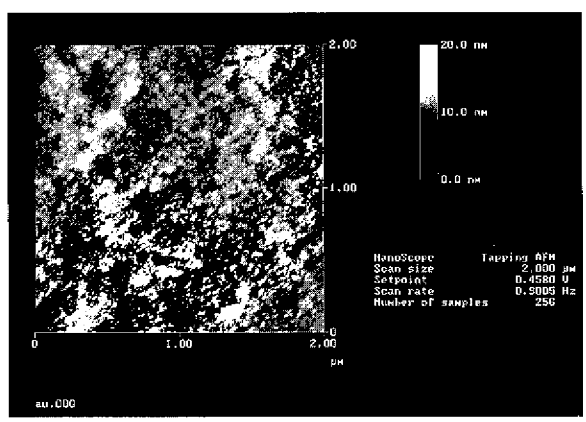


(b)

Fig. 8. 3D-AFM of the surface of a gold foil. (a) before coating; (b) after coating 6 minutes.

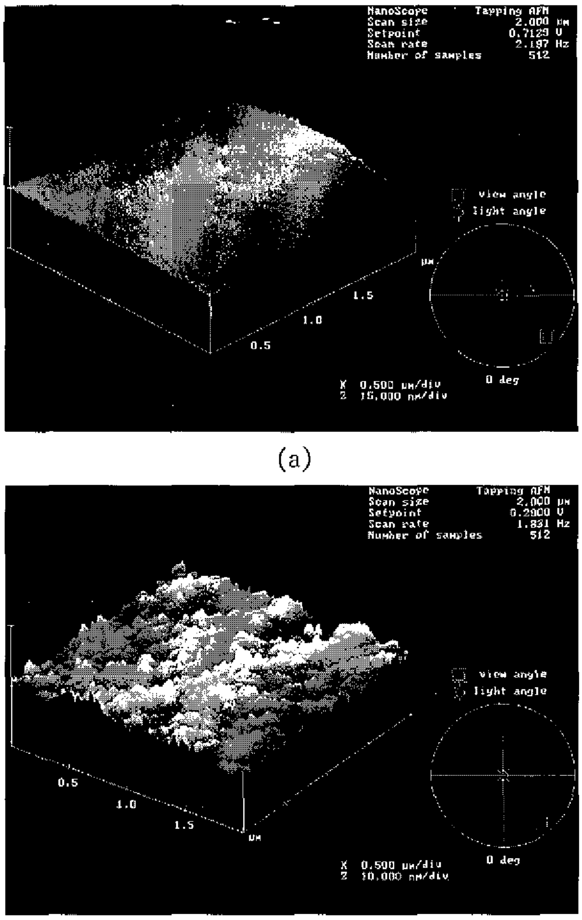


(a)



(b)

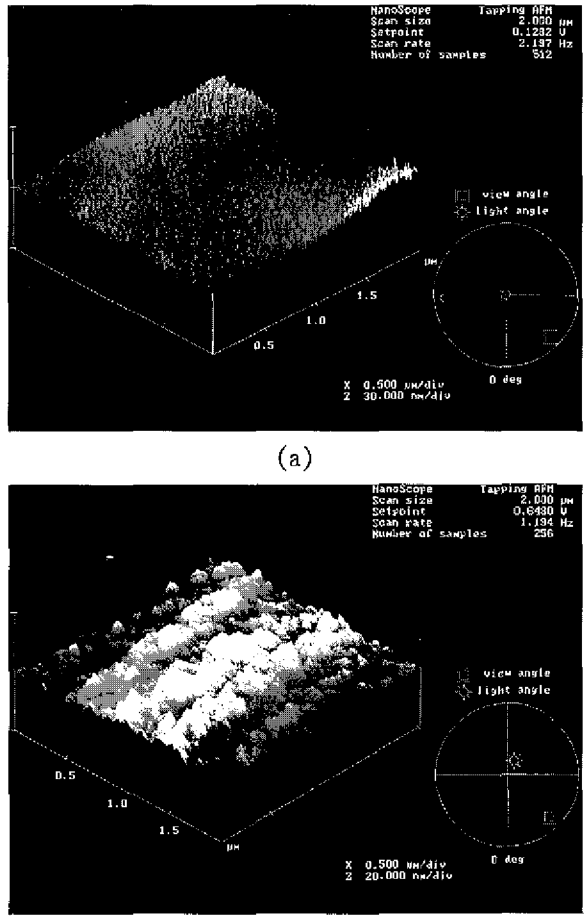
Fig. 9. 2D-AFM of the surface of a gold foil. (a) before coating; (b) after coating 6 minutes.



(a)

(b)

Fig. 10. Higher resolution 3D-AFM of the PMMA membranes prepared by (a) DGDE/water (b) acetone/water.



(a)

(b)

Fig. 11. 3D-AFM of the PMMA membrane and the gold foil after coating 30 seconds. (a) PMMA/DGDE/water (b) gold foil.

for the membranes prepared by PMMA/DGDE/water and PMMA/acetone/n-hexane, the distance between polymer aggregates (surface protrusions) is quite small and no obvious crevices on the surface were observed (Figs. 2a, 3a). For the other system (PMMA/acetone/water), large crevices among protrusions can be found (see Fig. 4a, 6a). For the two systems with small crevices, after sputter coating, the height of the surface protrusions increases (compare Figs. 2a with 2b, Figs 3a with 3b). However, for the system with large crevices (acetone/water), the most prominent effect of sputter coating on the surface structure is that the crevices have been filled with particles resulted from sputtering (compare Figs. 6a and 6b). On basis of the above observation, it can be deduced that sputter coating can definitely influence the membrane structure but the effect is different for different membranes. For membrane surfaces with small crevices among protrusions, it seems that the protrusions receive more coatings than the crevices, resulting in larger surface protrusions after sputter coating. On the other hand, for membrane surfaces with large crevices among protrusions, the crevices would be filled with the coating material, resulting in smaller crevices after sputter coating. For the former situation, after sputter coating, the basic characteristics of membrane surface structure might still be reserved but with larger variation in the surface height. However, for the latter situation, the original surface structure has been completely altered by the sputter coating process. On the basis of above discussion, it can be deduced that the sputter coating process could obscure the real membrane structure, especially for those membranes with rough surfaces in which the surface crevices might be filled with the coating material.

Effect of coating time

It should be noted that the coating time for all the cases discussed above is 6 minutes. Is the effect of metal sputtering less significant when the coating time is shorter? Figure 11 presents the AFM images of a PMMA membrane and the gold foil after a coating time of 30 seconds. It can be seen, for a coating time of just 30 seconds, the surface has in fact been altered, although it is less severe than a coating time of 6 minutes. When using SEM to analyze the structure of polymeric membranes, the coating time is usually longer than 30 seconds to have a conductive film on the membrane specimen. Therefore, for most situations, the effect of sputter coating on the observation of membrane structure is not negligible. This effect might not be important for low-resolution application; however, for studying fine membrane structures such as nodules, this effect should be carefully considered.

CONCLUSION

In this work, it was observed that the sputter coating process could produce coatings made up of distinguished particles, which should be the agglomerations of deposited material. The size of the agglomerated metal is on the same order of the size of nodules. Therefore, the sputter coating could affect the judgement on if nodules exist in a system or influence the determination of the size of nodules. In addition, it was found that, for membrane surfaces with small crevices among protrusions, it seems that the protrusions receive more coatings than the crevices, resulting in larger surface protrusions after sputter coating. On the other hand, for membrane surfaces with large crevices among protrusions, the crevices would be filled with the coating material, resulting in smaller crevices after sputter coating. Since the surface structures observed by SEM are the coated surface but not the real surface, one should be careful in interpreting the SEM micrographs, especially for fine membrane structures such as nodules.

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金屬濺鍍對高分子膜結構的影響

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摘　要

以電子顯微鏡觀察高分子膜結構時，需要在膜材上鍍一層金屬。本研究利用原子力顯微鏡來探討濺鍍前後高分子膜結構的差異，藉以評估濺鍍程序是否會對高分子膜結構的觀察產生影響。實驗結果顯示，濺鍍金屬層是由許多微小金屬顆粒所構成，而金屬顆粒的大小與高分子膜材粒狀結構的大小差不多（20 nm），因此濺鍍程序會對高分子膜中粒狀結構的觀察產生干擾。本研究之結果顯示：利用電子顯微鏡觀察高分子膜的細微結構（如粒狀結構）時，必須十分小心，因爲金屬濺鍍可能會改變這些細微結構。