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Self-assembled-monolayer film islands as a self-patterned-mask for SiO_2 thickness measurement with atomic force microscopy

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A novel method for measuring ultrathin (2–12 nm) SiO_2 film thickness is discussed. The process consists of: (1) formation of octadecyltrichlorosilane (OTS) self-assembled-monolayer (SAM) islands on SiO_2 of which thickness to be measured, (2) removal of the SiO_2 layers not covered by the OTS-SAM islands, and (3) measurement of the height difference between the etched and nonetched areas by atomic-force-microscopy. The OTS film is good resist against HF and its islands can be regarded as self-patterned-mask. Practical usefulness is demonstrated not only by the compatibility of the measured values but also by the short measurement period resulting from the directness of the method. © *1997 American Institute of Physics.* [S0003-6951(97)02125-6]

The shrinkage of ultralarge-scale integration (ULSI) circuit requires an ultrathin gate oxide as thin as 4 nm in 0.1 μm scale metal-oxide-semiconductor (MOS) devices which are expected to come out in the year 2007.[1] Since oxide thickness (T_{ox}) is one of the most important device parameters, the precise control of T_{ox} is the critical issue. T_{ox} is most commonly measured by nulling ellipsometry due to its easy sample preparation and short measurement time.[2] However, in the very thin thickness regime below 5 nm, accurate measurement of ellipsometric parameters, i.e., T_{ox} and the refractive index, becomes very difficult because these parameters couple each other and might be very different from those in the thick region. Although a simplified model using α-quartz refractive index has been proposed, its applicability to such a thickness regime has been questioned by previous papers.[3–8]

Alternative measurement techniques such as transmission electron microscope (TEM)[9,10] and x-ray photoelectron spectroscopy (XPS)[11] have a high sensitivity and can characterize T_{ox} in the ultrathin region. However, the TEM measurement requires an elaborate sample preparation and the nontrivial delineation of the interface such as SiO_2/Si or cap-material/SiO_2. Also, presumed values of electron mean free path in the SiO_2 layer used in XPS analysis are still controversial.

A method conveniently using atomic force microscopy (AFM) has been shown to be practical and useful for SiO_2 thickness measurement.[12] The typical process in this method is the following: (1) patterning of the mask on SiO_2 by photolithography, (2) chemical etching of SiO_2 layers not covered by the mask, (3) removal of the mask and the measurement of the height difference between the etched and the nonetched areas by AFM. However, this method requires too many processes for the routine measurement of T_{ox}. In addition, modification of T_{ox} due to deposition and removal of the mask may exist.

The concept of the technique presented in this paper is schematically shown in Fig. 1. This technique utilizes several characteristic features of self-assembled-monolayer (SAM) film which has been intensively studied these days.[13] First, some types of SAM film are known to be good resist for chemicals.[14–16] Second, the size of SAM islands can be controlled by the variation of time when the sample is dipped into solution.[17] Combining these features, SAM islands can be used as self-patterned mask (SPM) for chemical etching. Third, the growth of the SAM film is limited to a monolayer, beyond which no growth can proceed. This feature makes the height of the SAM islands uniform. These features enable one to eliminate many complex processes of pattern formation and removal of the mask required in the above-mentioned, conventional method. As shown in Fig. 1, AFM is used to determine the height difference (hereafter represented as Δd) of the areas with and without the SAM masks. It is expected that Δd will become larger with the increase of the etching time, t, during which the sample is dipped into HF. The time variation of Δd will be represented as $\Delta d(t)$. Since the etching rate for SiO_2 is much larger than that for Si, etching is considered to stop after the removal of the SiO_2 layer. So the $\Delta d(t)$ will saturate after a certain time, t_{sat}. The T_{ox} can be obtained by measuring $\Delta d(t>t_{sat})$ and $\Delta d(0)$, and by taking their difference, i.e., $T_{ox}=\Delta d(t>t_{sat})-\Delta d(0)$.

Experimentally, we use octadecyltrichlorosilane (OTS, $C_{18}H_{37}SiCl_3$), which has been shown to form the SAM film on the SiO_2 layer and also can serve as a mask for HF etching.[17] The SiO_2 film (~12 nm) is formed on Si(001) (p type, 10 Ω cm) by wet oxidation. Samples with various T_{ox}'s are prepared by etching-back the oxide by 1% HF

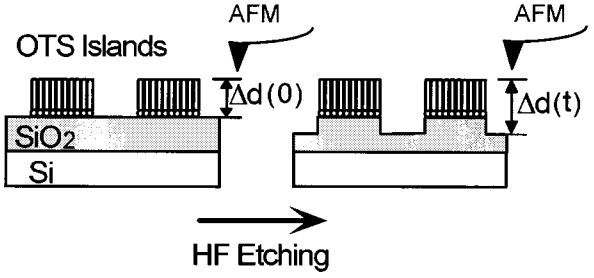

FIG. 1. Schematic drawing of thickness measurement of the SiO_2 film by AFM with the use of OTS-SAM islands. The $\Delta d(0)$ represents the height difference between the top of SAM islands and the exposed substrate before the etching of the sample by HF, and the variation of Δd as a function of dipping time, t, into HF is expressed as $\Delta d(t)$.

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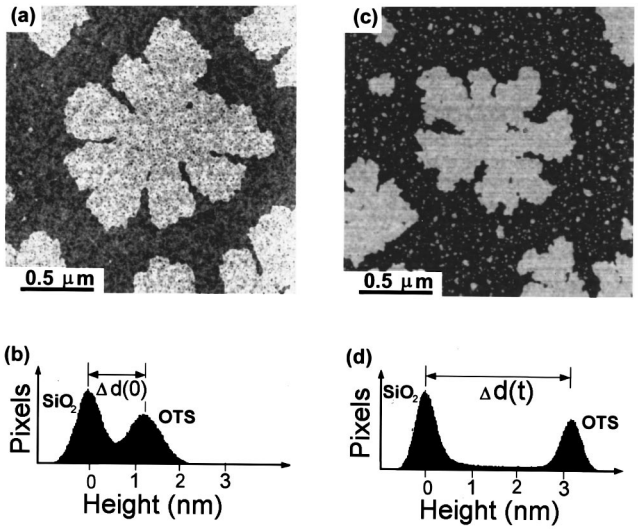

FIG. 2. (upper) AFM images of the SAM islands on the SiO_2 layer (thickness of $\sim$2.2 nm) before (a), and after (c) the HF etching of the sample (area $2\times2\ \mu m^2$) (lower). Histograms of the relative heights in the AFM image showing the height distribution of the OTS islands and substrate. The graphs (b) and (d) are corresponding to the images of (a) and (c), respectively.

with different etching periods. Then the OTS-SAM islands are formed by immersing the sample into a 1.0 mM solution of OTS (Aldrich) in a mixture of 8% $CHCl_3$+12% CCl_4+80% *n*-hexadecane (by volume) for 20 s at room temperature. Subsequently, the SiO_2 of nonmasked portion is etched by HF (HF:H_2O=1:20 by volume).

The height difference between the etched and nonetched area is measured by the AFM, Nanoscope IIIa (Digital Instruments, USA) with a 10 μm scanner. The height calibration is carried out by measuring the step height ($\sim$0.31 nm) of the wet-treated, atomically flat Si(111) surface.[18,19] The measured surface is imaged with the AFM tapping mode where the modulation amplitude and the frequency of the cantilever oscillation are 100 mV and 300 kHz, respectively. The reference thickness (T_{ellip}) is measured by ellipsometry with AutoEL III (Rudolph Research, USA) with fixed refractive index of 1.46. Identical wafers are also characterized by TEM with poly-Si capping.

Figure 2(a) shows a typical AFM image of the OTS-SAM formed on the sample of $T_{ellip}\sim$2.2 nm. Islands of OTS-SAM with a dendrite shape can be clearly seen, and SiO_2 bare surface is still visible between the islands. The size and the shape of the islands show strong dependence on the SiO_2 surface treatment prior to the OTS-SAM formation. This is consistent with the previous reports which showed that the existence of the substrate-bound water is necessary to obtain high density film.[20,21]

The height of the island in any area of the image can be evaluated by taking a single cross-sectional profile of the topography. However, in the present letter, we focus on measuring the averaged height of the entire islands with the following method to see the compatibility with other thickness-measurement techniques. First the background level of the AFM image is determined for all the areas which are not covered by SAM films. Second, after subtracting the background from the entire image, a histogram as a function of the relative height is plotted by counting the number of pixels in each division of height (0.1 nm). The result is shown in the Fig. 2(b). The two features corresponding to the substrate and the OTS islands appear with the separation of $\sim$1.1 nm with good reproducibility. Also, the two peaks have almost identical peak width. Since the peak width is correlated to the roughness of the surface, it may suggest that the measured roughness of the OTS-SAM island surface is governed by the roughness of the bottom SiO_2.

The measured $\Delta d(0)$, $\sim$1.1 nm, agrees with the previous reports,[16,22,23] but is smaller than the expected length of OTS molecule of $\sim$2.5 nm. The discrepancy has been attributed to the compression of the molecules by the pressure of the cantilever of the AFM.[14] For the purpose of this experiment, however, the stability of the height is most important. The measured Δd after dipping the sample into de-ionized water shows no variation from the one before the dipping, suggesting that the height of the OTS-SAM islands is not modified by the contact with water.

Figure 2(c) shows the image of the surface after dipping the sample into HF (HF:H_2O=1:20 by volume) for 30 s during which the SiO_2 layers not covered by the OTS-SAM is expected to be removed completely. The averaged size and the shape of the OTS-SAM islands are practically identical with the ones before the etching. Also there any additional big voids or any sign of peeling of the OTS-SAM cannot be seen, indicating the good resistance of the OTS-SAM islands against HF. Even for the thicker samples ($T_{ox}>$10 nm), the appearance of the OTS-SAM islands does not show big change after the etching process, suggesting the capability of this technique for the SiO_2 in the thicker film thickness regime.

The etching of the SiO_2 layers can be quantitatively seen in the height profile shown in Fig. 2(d). The two features corresponding to the substrate and the OTS-SAM islands are much more separated than those in Fig. 2(b), as a result of the etching of the SiO_2 layers. However, the widths of both features do not show any significant change from the ones in Fig. 2(b), indicating no degradation of the OTS-SAM islands. From Figs. 2(b) and 2(d), T_{ox} can be determined as $\Delta d(t>t_{sat})$-$\Delta d(0)$=3.2−1.1=2.1 nm.

Figure 3 shows the observed $\Delta d(t)$ for samples with three different T_{ox} as a function of etching time, *t*, into HF. The $\Delta d(t)$ varies very smoothly as a function of *t*, and it saturates beyond a certain etching time ($\sim$20 s). The fluctuation of $\Delta d(t)$ after the saturation is within 0.1 nm, indicating a high reproducibility of this technique and the stability of the OTS-SAM film. The three curves are on the identical straight line for the first 10 s. This is reasonable since HF etching should proceed with an identical rate for the three surfaces of the SiO_2. However, the apparent etching rate, 0.12 nm/s, is much slower than the one expected from the usual etching rate by HF of this concentration, 0.25 nm/s.[24] After this stage, an acceleration of etching rate in all curves can be seen. Although the origin of those phenomena are not perfectly understood at this point, it may suggest that this technique is useful not only for T_{ox} determination but also for revealing the properties of SiO_2 near the SiO_2/Si interface.

Finally, we will show comparison of T_{ox} measured with

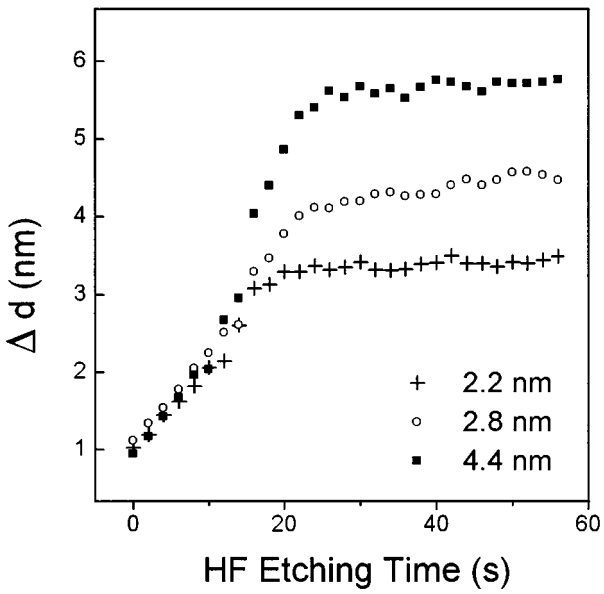

FIG. 3. Plots of the depth variation as a function of the HF etching time. The concentration of HF is HF:H_2O=1:20 by volume. The three curves correspond to the samples with SiO_2 thickness of 2.2, 2.8, and 4.4 nm which were determined by ellipsometry using a fixed value of the refraction index, 1.46.

various techniques: ellipsometry, TEM, and the present SAM-SPM method. The result is summarized in Table I. It can be immediately noticed that T_{ox} determined by the SAM-SPM method shows very good agreement with the ellipsometry measurement up to $T_{ox}\sim 12$ nm. There has been discussion that T_{ox} measured by ellipsometry with a fixed refraction shows thicker value than the one obtained by TEM.[5] However, the coincidence of the measured values by ellipsometry and the SAM-SPM method may call attention to the validity of the TEM measurement, such as the image averaging effect caused by the electron beam which was pointed out by a comparison between the TEM and the cross-sectional STM images.[25]

TABLE I. Comparison of the thickness measured by various techniques. Ellipsometry are used with the fixede refractive index, 1.46. TEM samples are capped with poly-Si.

Sample No.	Ellipsometry (nm)	TEM (nm)	SAM-SPM (nm)
1	2.2	0.8	2.1
2	2.8	1.8	3.2
3	4.4	2.9	4.7
4	11.9	8.8	12.2

In summary, we have shown the feasibility of the use of OTS-SAM for the direct and precise measurement of SiO_2 thickness. It was found that the OTS-SAM on SiO_2 forms islands which can be a good resist against HF etching. Thus, it is possible to form one area where SiO_2 is removed and another where SiO_2 remains unperturbed after the etching. Since the OTS islands have a uniform thickness, $\Delta d(0)$, the height difference of these two areas, $\Delta d(t)$, subtracted from $\Delta d(0)$, indicates the thickness of SiO_2. The measured SiO_2 thickness showed good agreement with the ellipsometry measurement for the range of 2–12 nm. It was shown that this technique can be a good tool not only for the thickness measurement in the ultrathin film but also for the SiO_2 property investigation near the interface.

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[1] See for example, *The National Technology Roadmap for Semiconductors* (SEMATECH Inc., Austin TX, 1994).
[2] R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, New York, 1977).
[3] E. A. Taft and L. Cordes, J. Electrochem. Soc. **126**, 131 (1979).
[4] D. E. Aspnes and J. B. Theeten, Phys. Rev. Lett. **43**, 1046 (1979).
[5] A. H. Carim and R. Sinclair, J. Electrochem. Soc. **134**, 741 (1987).
[6] A. Kalnitsky, S. P. Tay, J. P. Ellul, S. Chongsawangvirod, J. W. Andrews, and E. A. Irene, J. Electrochem. Soc. **147**, 234 (1990).
[7] T. S.Chao, C. L. Lee, and T. F. Lei, J. Electrochem. Soc. **138**, 1756 (1991).
[8] G. E. Jellison, Jr., J. Appl. Phys. **69**, 7627 (1991).
[9] J. Blanc, C. J. Buiocchi, M. S. Abraham, and W. E. Ham, Appl. Phys. Lett. **30**, 120 (1977).
[10] O. J. Krivanek and J. H. Mazur, Appl. Phys. Lett. **37**, 392 (1980).
[11] F. J. Grunthaner and J. Maserjian, in *The Physics of SiO_2 and its Interfaces*, edited by S. T. Pantelides (Pergamon, New York, 1978).
[12] T. Ohmi and S. Aoyama, Appl. Phys. Lett. **61**, 2479 (1992).
[13] A. Ulman, *An Introduction to Ultrathin Organic Films from Langmuir–Blodgett to Self-Assembly* (Academic, CA, 1991).
[14] M. J. Lercel, R. C. Tiberio, P. F. Chapman, H. G. Craighhead, C. W. Sheen, A. N. Parikh, and D. L. Allara, J. Vac. Sci. Technol. B **11**, 2823 (1993).
[15] S. R.Waseman, G. M. Whitesides, I. M. Tidswell, B. M. Ocko, P. S. Pershan, and J. D. Axe, J. Am. Chem. Soc. **111**, 5852 (1989).
[16] R. C. Tiberio, H. G. Craighead, M. Lercel, T. Lau, C. W. Sheen, and D. L. Allara, Appl. Phys. Lett. **62**, 476 (1993).
[17] M. J. Lercel, G. F. Redinbo, H. G. Craighhead, C. W. Sheen, and D. L. Allara, Appl. Phys. Lett. **65**, 974 (1994).
[18] G. S. Higashi, Y. J. Chabal, G. W. Trucks, and K. Ragavachari, Appl. Phys. Lett. **56**, 656 (1990).
[19] T. Komeda, Y. Morita, and H. Tokumoto, Surf. Sci. **348**, 153 (1996).
[20] J. B. Brzoska, I. Ben Azouz, and F. Rodelez, Langmuir **10**, 4367 (1994).
[21] D. L. Allara, A. N. Parikh, and F. Rodelez, Langmuir **11**, 2357 (1995).
[22] M. Pomeranz, A. Semmuler, L. Netzer, and J. Sagiv, Thin Solid Films **132**, 153 (1985).
[23] A. Takahara, K. Kojio, S.-R. Ge, and T. Kajiyama, J. Vac. Sci. Technol. A **14**, 747 (1996).
[24] H. Kikuyama, M. Waki, M. Miyashita, T. Yabune, N. Miki, J. Takano, and T. Ohmi, J. Electrochem. Soc. **141**, 366 (1994).
[25] R. M. Feenstra, E. T. Yu, J. M. Woodall, P. D. Kirchner, C. L. Lin, and G. D. Pettit, Appl. Phys. Lett. **61**, 795 (1992).