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Influence of hydrogen on the structure of amorphous carbon

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We have studied the influence of hydrogen on the structure of *a*-C:H films (produced by sputtering) by measuring the stress, hardness, and Raman spectrum as a function of the hydrogen concentration C_H. Addition of hydrogen, on the one hand, reduces the stress and hardness, and on the other hand, reduces the intensity ratio (I_D/I_G) of the Raman *D* to *G* line. Discontinuous change of both stress and I_D/I_G, and a minimum of the *G*-line full width at half maximum have been observed at $C_H \approx 32.5$ at. %. Scanning-electron-microscopy analysis has been used to verify the stress transition. The role of hydrogen is discussed.

I. INTRODUCTION

Films of hydrogenated amorphous carbon (*a*-C:H) are of considerable interest due to their hardness, chemical inertness and optical transparency. Utilization of these films for various applications has promoted intense research in this field in recent years.[1–11] Considerable uncertainty concerning the microscopic origins of these interesting properties seems to originate from the presence of two different bonding configurations, namely, sp^3 and sp^2. In the sp^3 bonding configuration, carbon atoms are tetrahedrally bonded as in diamond. In the second case, carbon is trigonally bonded as in graphite. Hydrogen, incorporated in these structures, plays a crucial role in the stabilization of the tetrahedrally coordinated carbon atoms, and produces a wide variety of materials with different properties.

The detailed structure of the bonding network in amorphous carbons is still under study. However, some theoretical models have been proposed by several authors.[5–11] Angus and Jansen[6] suggest a random covalent network model and find a relation between hydrogen concentration C_H (at. %) and the ratio of sp^3 to sp^2 bondings: $Csp^3/Csp^2 = (6C_H - 1)/(8 - 13C_H)$ valid for *a*-C:H with a fully constrained hydrocarbon network. In the two phase model of Robertson *et al.*,[5,10] the amorphous carbon consists of sp^2-bonded planar carbon clusters (fused sixfold rings) embedded in a randomly oriented tetrahedrally sp^3-bonding matrix. The matrix connectivity largely controls the mechanical properties, while the rings control the band gap. Tersoff has made a theoretical study of the structural properties of sp^3-bonded *a*-C:H. He shows that without hydrogen, the material is very hard. It is a highly strained ordinary sp^2-bonded *a*-C. Increasing the hydrogen content favors the sp^3 bondings and reduces the internal strain.

Different authors have studied the mechanical properties of *a*-C:H films, deposited by plasma assisted chemical vapor deposition (CVD), in relation to the substrate bias voltage V_b. Dekempeneer *et al.*[3] have found that the stress and hardness reach a maximum at about $V_b = 200$ V. The hydrogen concentration of their samples was about 30 at. %, nearly independent of the different bias voltages. Tamor, Vassell, and Carduner[4] have also observed a maximum of stress and hardness at $V_b \approx 200$ V. But more important is that a maximum fraction of unprotonated sp^3 bonding is observed at about $V_b = 200$ V by nuclear magnetic resonance spectroscopy.

It is known that Raman spectra are very sensitive to changes that disrupt the translational symmetry and are therefore useful for studying disorder and crystallite formation in thin a-C:H films. Raman spectra of amorphous carbon films have been analyzed by several authors.[12–16] The Raman spectrum of amorphous carbon has a broad peak, namely, the *G* line, at about 1580 cm^{-1} (position of the Raman line of the crystalline graphite). The striking feature of these Raman spectra is the appearance of another peak at about 1350 cm^{-1}, namely, the *D* line. This peak is not due to sp^3 sites, but is attributed to an activated intralayer "disorder mode" of microcrystalline graphite. Its intensity depends inversely on the microcrystallite diameter.[12,14,15]

Despite its importance, the influence of hydrogen on the structure of amorphous carbon, which is revealed by microstructure order and mechanical properties such as stress and hardness, is not quite clear.

In this paper, we present the experimental results of a study of the influence of hydrogen on internal stress, hardness and Raman spectra of *a*-C:H films prepared by rf-magnetron sputtering. All parameters but the gas ratio $C_2H_2/(C_2H_2+Ar)$ which controls the H concentration, were kept constant during the *a*-C:H film depositions. Our results show that an increase of hydrogen concentration reduces the internal stress from compressive to slightly tensile values, increases the sp^2-bonded carbon clusters sizes, reduces the hardness, and suggest that an important structures modification occurs as C_H becomes larger than 32.5 at. %.

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II. EXPERIMENTAL DETAILS

a-C:H films have been prepared by rf-magnetron sputtering of a graphite target in a gas mixture of Ar and C_2H_2 at a total pressure 2.10^{-2} mbar. Two-inch *c*-Si(111) wafers were used as substrates. The deposition temperature was kept at ~120 °C. The bias of the cathode was 450 V. All samples were prepared under the same condition except that the C_2H_2 concentration $[C_2H_2/(C_2H_2+Ar)]$ varied from 0.25% to 5%, corresponding to a C_H variation from 26.8% to 36.7%. The film thicknesses are in the range 2 to 14 μm. The hydrogen concentration profiles of *a*-C:H films were measured by Elastic Recoil Detection Analysis (ERDA). It consists of measuring the energy spectrum of protons which have been elastically hit by α-particles (produced by our Van de Graaff accelerator) and recoil in the forward direction. The proton energy spectrum is a function, in particular, of the hydrogen concentration profile to be determined. The α-beam intensity was determined by Rutherford backscattering spectroscopy (RBS) of α's scattered by C atoms at 71.6° [90° c.m.] At this angle the $C(\alpha,\alpha)$ cross section is essentially of the Rutherford type.[17] The experimental setup is described elsewhere in detail.[18]

In all measured samples, the hydrogen atomic concentration $C_H = H/(H+C)$ was found to be independent of the depth. The internal stress of *a*-C:H films, σ, was determined from the curvature of coated silicon substrate, by using the Jaccodine and Schlegel formula:[19]

$$\sigma = \frac{Es}{6(1-Vs)} \frac{d_{si}^2}{d_f} \frac{1}{R} , \tag{1}$$

where, Es is the Young's modulus (1.88×10^{12} dyne/cm^2), Vs is Poisson's ratio (0.181) of the *c*-Si(111) substrate,[20] d_{si} and d_f are the substrate and *a*-C:H film thickness, respectively, and R is the radius of curvature which was measured by a stylus profilometer. The curvature of the wafers before film deposition was found to be negligible.

The Raman spectra measurements were performed at room temperature on a prototype compact Raman spectrometer (*RENISHAW*) using the 6328 Å line of a He-Ne laser with an output energy of 30 mW. The resolution of the Raman spectrum is about 2 cm^{-1}. The hardness of some samples has been measured by using an ultramicrohardness tester (CSEM). This instrument is based on a nanoindentation technique, and is especially used in thin film mechanical property measurements.

III. RESULTS

Figure 1 shows the film internal stress, σ, versus the hydrogen concentration, C_H, in the film. Below 32.5 at. %, the stress is compressive, and decreases as C_H increases. A drastic drop of σ occurs when C_H reaches about 32.5 at. %. Above this limit, σ becomes slightly negative which means that the stress becomes tensile. Further increase of C_H maintains σ at tensile values. The microhardness of two typical *a*-C:H samples has been measured. We found 1.21 and 0.58 GPa with $C_H = 26.8$ and 36.3 at. %, respectively.

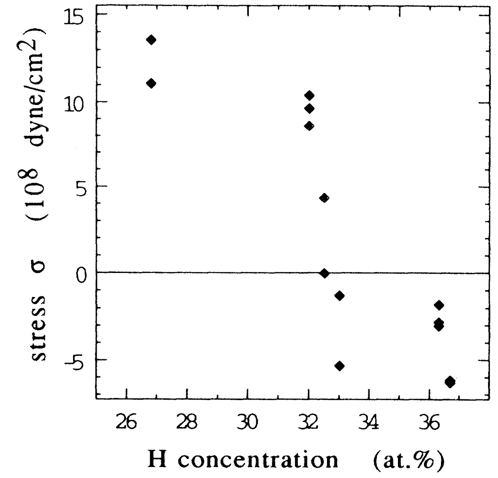

FIG. 1. Stress of the *a*-C:H films, σ, vs hydrogen atomic concentration, C_H.

In order to verify the stress transition, we have analyzed the surface morphology by scanning-electron microscopy (SEM), Fig. 2 shows the evolution of the surface morphology of our films with different hydrogen concentrations. They show that the film surface morphology, smooth at low hydrogen content, becomes rough and unhomogeneous as C_H goes over 32.5 at. % [see Figs. 2(d) and 2(e)]. No evidence of pealing or cracking has been observed.

The small stress values indicate that the structure is soft. The rough and unhomogeneous morphology in the samples with tensile stress [Figs. 2(d) and 2(e)] suggests that the structure is somewhat polymerlike, although the hydrogen content is in an intermediate range (26.8~36.3 at. %).

The Raman spectrum measurements show that there are two major peaks. One is the *D* line in the range of 1330–1366 cm^{-1}, the other one is the *G* line in the range of 1584–1593 cm^{-1}. All Raman spectra could be fitted well by two major Gaussian peaks (*D* and *G* lines), and two "parasitic" Gaussian lines at about 1200 and 1550 cm^{-1}, respectively, superimposed to a linear background. Figure 3 shows a typical measured Raman spectrum fitted by the Gaussian lines. In Fig. 4, the intensity ratio of the *D* to the *G* lines, I_D/I_G, is plotted as a function of C_H. The positions of the *D* and *G* lines, and the full width at half maximum (FWHM) of the *G* line are given in Table I. The latter is known to increase with the bond-angle disorder.[12,14,15] As one can see, the value of I_D/I_G decreases as the hydrogen content rises, indicating growth of the sp^2 cluster size L_a. L_a(Å) was estimated (see Table I), by using the relation, $L_a(\text{Å}) = 44(I_D/I_G)^{-1}$.[15] Again we have observed that I_D/I_G abruptly decreases, when the hydrogen concentration reaches 32.5 at. %. Furthermore the *G* line width (i.e., FWHM of *G* lines), reflecting the cluster intralayer disorder, reaches a minimum at $C_H = 33$ at. % (see Table I). This suggests that under our amorphous carbon deposition condition, an important structure change occurs when C_H exceeds 32.5 at. %.

IV. DISCUSSION

Our results are partially in agreement with Tersoff's theoretical results.[8] Increasing hydrogen content indeed reduces the internal stress and hardness of our *a*-C:H films. However, we do not think that the carbon atoms of the film are nearly ideal sp^3 bonded as predicted by the Tersoff's computed model for a H content above 25 at. %. Indeed, the Raman spectrum measurements show the existence of the two major *D* and *G* lines, indicating that the films consist of the sp^2 bonded, planar carbon

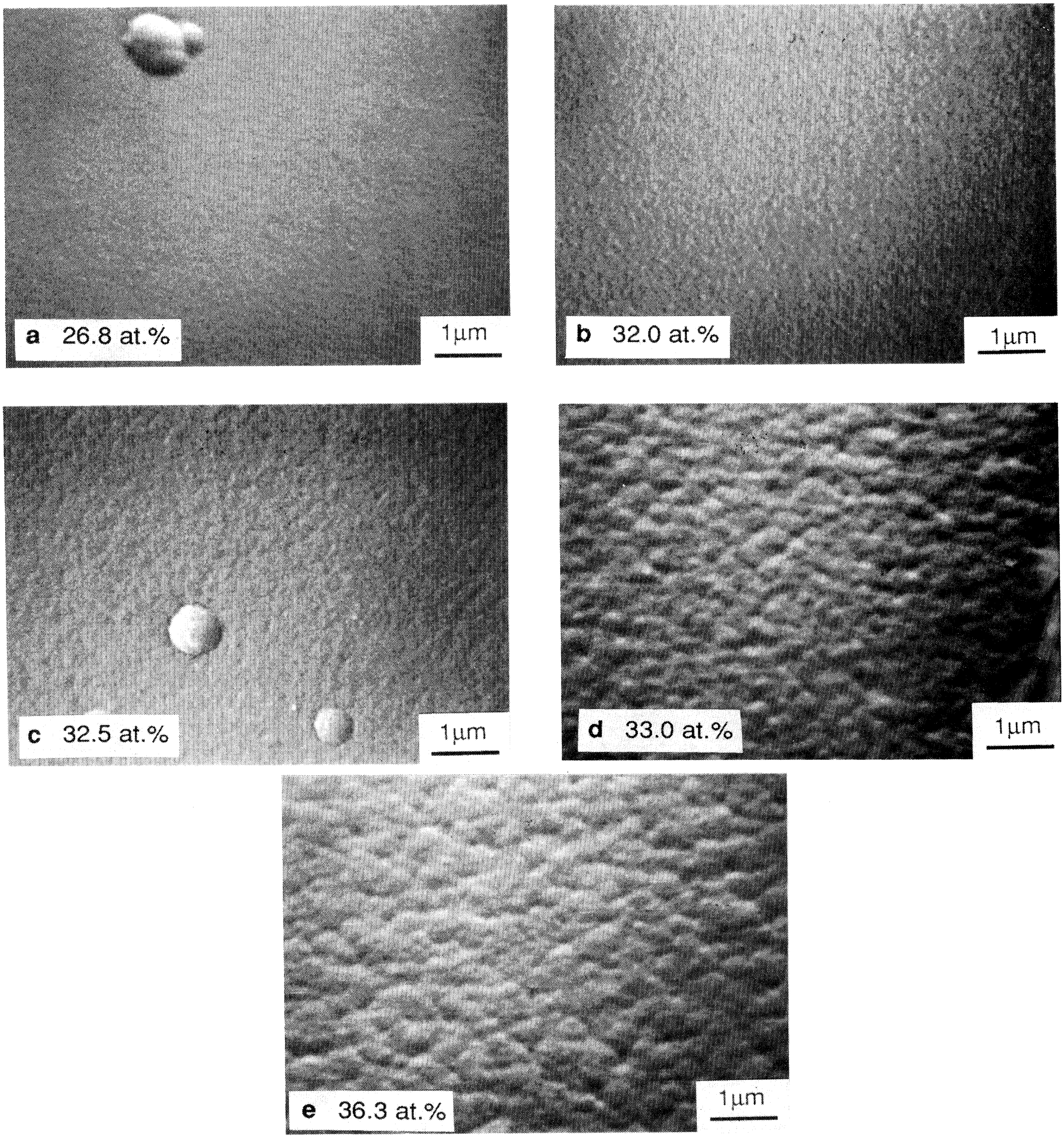

FIG. 2. SEM micrograph of the surface of *a*-C:H films with different C_H.

TABLE I. P_D,P_G: positions of the Raman D and G lines, respectively; $\Delta\nu$: G line FWHM; L_a: cluster size.

C_H (at. %)	P_D (cm^{-1})	P_G (cm^{-1})	$\Delta\nu$ (cm^{-1})	L_a (Å)
26.8	1330	1593	66	14.8
32.0	1332	1592	64	16.2
32.5	1330	1590	63	16.4
33.0	1331	1587	62	16.8
33.0	1333	1585	61	17.4
36.3	1335	1584	71	18.5
36.7	1366	1585	93	18.8

clusters.

According to the random covalent networks model of Angus and Jansen, when hydrogen concentration is in the range of 16.7 at. % to 61.5 at. %, a fully constrained random hydrocarbon network consisting of both sp^3 and sp^2 bonding can exist in *a*-C:H. The model predicts that increasing the hydrogen content in this range will reduce the internal stress of the film, since the addition of hydrogen reduces the average coordination number, thereby reducing the number of bonding constraints per atom. Therefore one can expect a monotonic decrease of the internal stress when C_H increases. However our results show that, even in the intermediate H constant range, the compressive stress is small and vanishes when C_H becomes larger than 32.5 at. %, well below the 61.5 at. % limit above which the Angus and Jansen model predicts that hydrocarbon network is underconstrained. This discrepancy in the intermediate hydrogen concentration range means that the structure of our sputtered *a*-C:H films cannot be described by a full constrained hydrocarbon network model.

The results of our Raman and stress measurements suggest that the structure of our *a*-C:H films consists mainly in sp^2 clusters. These connect to each other by sp^2 and sp^3 bonds, thus forming a matrix of sp^2 clusters whose boundaries are partly decorated by hydrocarbon. The more hydrogen is introduced *during* film deposition (or the higher C_H), the large are the sp^2 clusters (I_D/I_G decreases), the larger is their intralayer order ($\Delta\nu$ decreases) and, therefore, the larger is the strain relief. We think that as C_H increases the cluster boundary decoration extends so that hydrocarbon networks develop. At C_{Hc} (in our case 32.5 at. %) some of these networks "percolate" and fracture the matrix into cluster groups connected loosely to each other. In other words, the cluster groups are separated by hydrocarbon. This process can explain the sharp drop of stress. Subsequent increase of hydrogen content causes polymerization in the cluster group boundary regions resulting in a stress reversal which thus becomes tensile. We think that the critical H content can exist only if the *a*-C:H structure consists mainly in sp^2 clusters and that it could be varied by the deposition condition. In fact, if the optimal number of unhydrogenated sp^3 bonds has been produced and the sp^2 clustering has been reduced to a minimum by optimization of the deposition condition, a fully constrained random hydrocarbon network can be obtained, resulting in hard and highly stressed *a*-C:H. This has been confirmed by Dekempeneer *et al.*[3] and Tamor, Vassell, and Carduner.[4] They have found that, under the deposition condition of plasma enhanced CVD with optimal bias voltage ($\approx$200 V), the film structure was composed of an overconstrained random extended network in which only small graphitic clusters are captured, with a maximum number of unhydrogenated sp^3 bonds, and that the *a*-C:H has maximum stress and hardness, even if the *a*-C:H contains 30 at. % hydrogen.

Our explanation of the results presented here is partially similar to the two phase model proposed by Robertson *et al.*, in the sense that *groups* of sp^2 clusters instead of

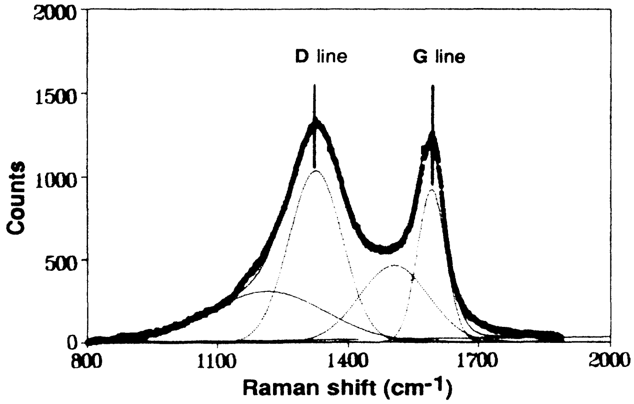

FIG. 3. A typical Raman spectrum fitted by 4 Gaussian functions.

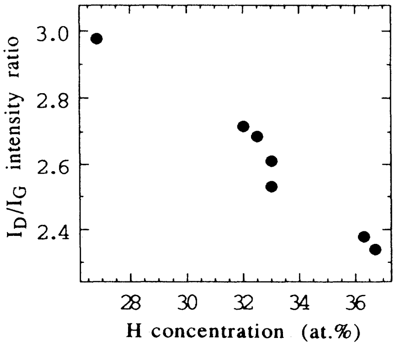

FIG. 4. Intensity ratio, I_D/I_G of the Raman D line to G line vs the hydrogen atomic concentration, C_H.

sp^2 clusters alone, are connected by a soft or polymerlike hydrocarbon network instead of by pure sp^3 carbon network.

V. SUMMARY

In summary, we have studied the hydrogen influence on the structure of *a*-C:H film (produced by sputtering) by measuring the stress, hardness and Raman spectrum in relation to hydrogen concentration. The addition of hydrogen reduces the stress, the hardness, and the intensity ratio (I_D/I_G) of the Raman D to G line. The rapid change of both stress and hardness and a minimum of G line FWHM, at $C_H \sim 32.5$ at.%, have been observed. We suggest that a critical value of hydrogen concentration C_{Hc} exists above which a polymerlike structure develops in a "percolating" way which can explain the sharp decrease of stress and the modification of the film morphology.

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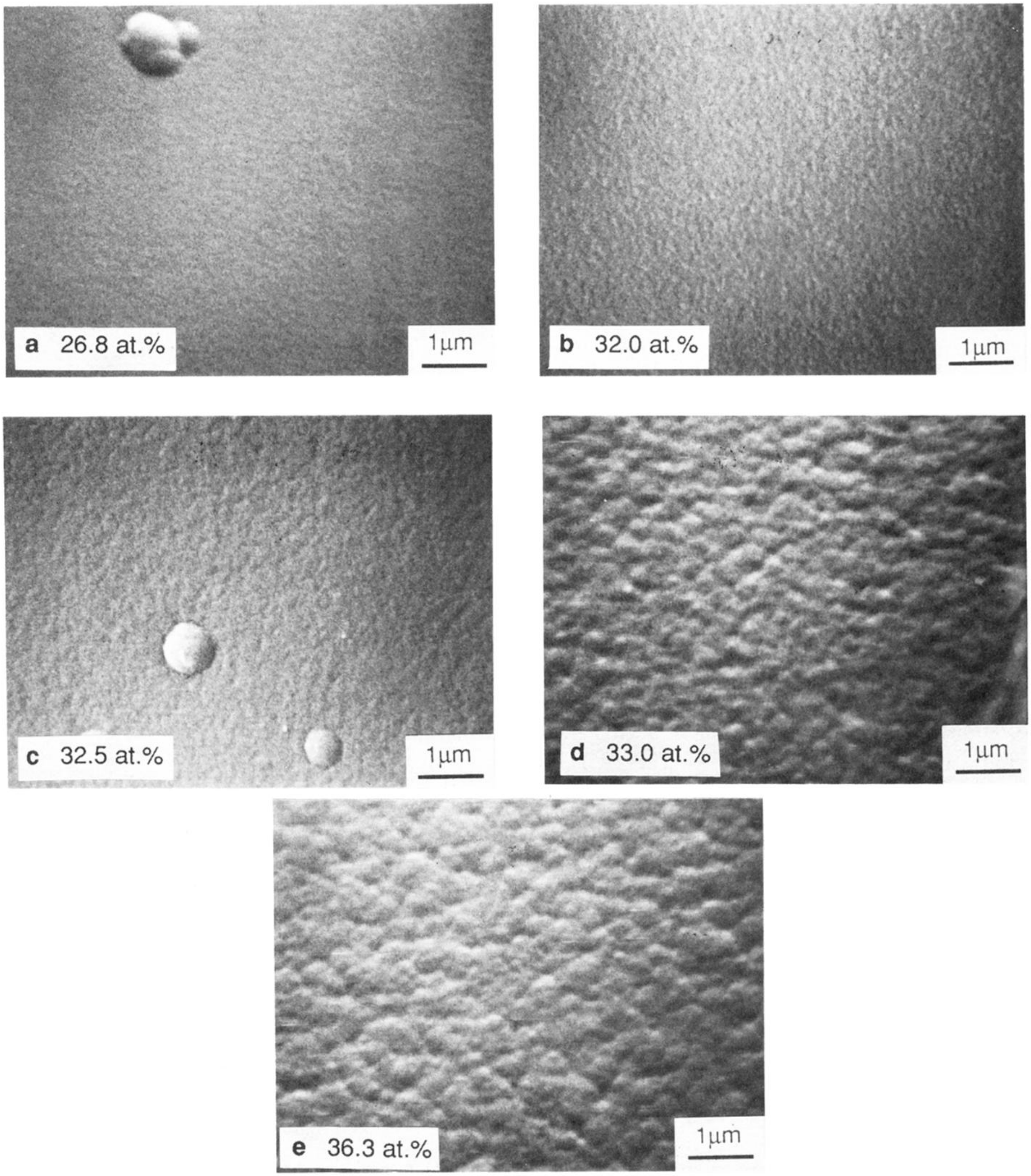

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