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**ATOMIC FORCE MICROSCOPE STUDIES OF CuCl ISLAND FORMATION ON CaF₂ (111)
SUBSTRATES**

by

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Atomic Force Microscope Studies of CuCl Island Formation on CaF₂(111) Substrates

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Abstract

We have grown by molecular beam epitaxy (MBE) CuCl thin films at various thicknesses and substrate temperatures on CaF₂(111) substrates. Atomic Force Microscope (AFM) topographs reveal that islanding is the dominant growth mechanism. Quantitative analysis of the AFM data enabled us to determine the amount of the substrate remaining exposed after the deposition as well as the total amount of CuCl deposited. We calculated the reciprocal-space height correlation function, $\langle |h(\mathbf{q}, t)|^2 \rangle$, for each of our films and compared them to the predictions of the Shadowing Growth Theory, which enabled us to extract the important kinetic parameter of surface diffusion length for the growth condition of each of the four films.

INTRODUCTION

We are interested in the optical properties of CuCl, a semiconductor with a direct bandgap of 3.4 eV, because of its non-linear optical properties. CuCl excitons have a binding energy of 200 meV, which is the highest among all zincblende semiconductors. The extremely high oscillator strength for exciton creation is responsible for optical bistability in CuCl. Previous research in our group has shown that the photoluminescence lifetimes of *quantum-confined* CuCl excitons are very short (<40 ps) [1,2], which makes CuCl thin films potential building blocks for a fast optical switching device. CaF₂ was chosen as the substrate and the barrier material for the quantum wells because of its low lattice mismatch with CuCl (<1 %) and its high bandgap (ca. 10 eV). Since the optical characteristics of these quantum wells depend strongly on their thickness, our ultimate goal is to grow CuCl quantum wells that are *both* thin and uniform. However, two factors have conspired to prevent us from doing so. At substrate temperatures below 110°C, the deposited CuCl always yielded spotty Reflection High-Energy Electron Diffraction (RHEED) patterns -- an indication of islanding; but at substrate temperatures higher than 110°C, the CuCl has a very low sticking coefficient to the CaF₂ surface and thus films will not grow.

The goal of this study is to understand better the *kinetics* behind island formation in film growth. Both thermodynamics *and* kinetics play key roles in determining how film growth proceeds, especially in island formation. The thermodynamics behind film growth is reasonably well understood, at least on a theoretical level: the surface and interfacial energies of the substrate and the deposited material dictate whether growth proceeds in the Franck-van der Merwe mode (layer-by-layer), the Stranski-Krastanov mode, or the Volmer-Weber mode (the latter both islanding) [3]. Kinetics plays an equally important role in film growth, since island formation is limited by surface diffusion. Yet, our theoretical understanding the kinetics of film growth is still limited. A macroscopic description began in the 1950's. Konig and Helwig were the first to point out the geometrical shadowing effect [4]. Protruding parts of a surface shield lower-lying regions and enhance the roughness of a surface as growth proceeds. This roughening mechanism competes with various sintering or smoothing mechanisms, the most prominent one being

surface diffusion, as discussed by Herring [5]. The Shadowing Growth Theory advanced by Karunasiri, Bruinsma, and Rudnick [6-8] accounts for the stochastic nature of deposition by including a shot noise term in a linear response treatment that includes both shadowing and diffusion. In this work, we utilized an atomic force microscope (AFM) to obtain quantitative topographs of our CuCl thin films grown on CaF₂(111) substrates and then utilized the Shadowing Growth Theory as a framework to extract kinetic information from our experimental data.

EXPERIMENTAL PROCEDURE

All samples analyzed in this work were grown at RIKEN in an Irikoken Molecular Beam Epitaxy (MBE) chamber equipped with a quartz crystal deposition monitor, RHEED, CuCl and CaF₂ Knudsen cells, and other standard ultra high vacuum (UHV) accessories. All four films used in this study were deposited on CaF₂(111) substrates that had been rinsed in methanol and sonicated in trichloroethylene prior to loading. After being loaded into the chamber, all four substrates were annealed in UHV at 800°C, as determined by a thermocouple on the sample holder. After at least 2 hours, the substrates displayed streaky RHEED patterns, which indicated that the surfaces were well ordered and fairly flat. During growth of the CuCl films, two of the substrates were held at 110°C and the other two at 80°C (denoted by the prefixes A and B, respectively, in the sample labels). At each growth temperature, one substrate (labeled with the suffix 1) received a molecular fluence sufficient to deposit a uniform CuCl film 60 Å thick and the other (labeled with the suffix 2) 120 Å, as determined by the quartz crystal monitor. The flux of the CuCl beam was maintained to deposit an approximately 25 Å thick layer per minute for all four substrates. Each film yielded a spotty RHEED pattern during growth. After growth was complete, the films were withdrawn from the chamber, quickly transferred into a desiccator, and then transported to UCLA for further analysis. The AFM investigations of the films were made in air at room temperature with a Digital Instruments Nanoscope II atomic force microscope at the Jet Propulsion Laboratory.

RESULTS

The AFM topographs of the four films, which are 50,000 Å by 50,000 Å scans with the z scale magnified 10 times compared to the x and y scale to enhance the surface features, are shown

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in Fig.1. It is clear from these topographs that islanding is the predominant growth mode for CuCl on CaF₂ (111). In the films grown at 110°C, the islands are larger and fewer in numbers than those in their 80°C counterparts.

For Film A1, which had the nominal 60 Å average thickness, the flat areas around the islands are probably the exposed CaF₂ substrate, and the abundance of these flat areas can be attributed to the strong islanding tendency of the deposited CuCl. The islands on Film A1 are typically 300 Å high and 3000 Å in diameter; many have cubic corners that may be the result of faceting. For Film A2, the nominal 120 Å film, the islands are typically twice as high and wide as those in Film A1. Film A2 appears to have far more than twice the amount of deposited material as Film A1 does, which suggests CuCl has a higher sticking coefficient on itself than on CaF₂. The islands on Film A2 also have fewer sharp corners.

For the 80°C films, the appearance of the islands is quite different. Here the islands are smaller and more numerous, and they are located much closer to each other. Unlike the topographs for the two 110°C films, which are quite different from each other, these two topographs are very similar and not easily distinguishable. Only after close examination can one tell that the islands on the nominal 120 Å film (B2) are larger than those on the nominal 60 Å film (B1).

DISCUSSION

Height distribution function. In order to quantify our analysis, we calculated the height distribution function for each of the topographs, as shown in Fig.2. The height distribution function, $n(H)$, of an AFM topograph is the number of points in the topograph that has a given height H . For all four topographs, the distribution function contains two peaks: a sharp one that defines $H=0$ and a broad one that is an average over the island sizes and shapes centered at a higher H . The $H=0$ peak is a result of the exposed substrate, since the substrate is known to be flat from the RHEED patterns and the AFM topograph must contain a large number of points at that height given the amount of material deposited and the size of the islands. The width of this peak is caused by a combination of the corrugations on the substrate surface itself and the tilting of the surface with respect to the x-y plane as defined by the AFM. The widest Full Width Half

Maximum (FWHM) is only 50 Å, which is very small compared to a scanned area that spans 50,000 Å. Of special interest is the fact that parts of Film A2 are thicker than 1,000 Å, which is an illustration of the strong thermodynamic driving force behind the islanding in our system.

From the height distribution function, we are able to calculate the average thickness T of the film, which is the thickness of the deposited material if it were spread evenly across the surface:

$$T = \frac{\sum_H H \cdot n(H)}{\sum_H n(H)} \quad (1)$$

The average film thickness for each film is listed in Table 1. It is not clear why they are significantly larger than those predicted by the quartz crystal monitor data. One possibility is that the sticking coefficients for CuCl on gold (the coating for the quartz crystal), on CaF₂(111), and on CuCl differ significantly; another possibility is that the CuCl islands may contain defects such as vacancies, which would reduce the density of the deposited CuCl compared to bulk material. However, we have also grown 5,000 Å thick CuCl films on CaF₂(111) substrates at the same substrate temperatures and x-ray diffraction studies have shown those films to be epitaxial with an essentially bulk lattice constant.

The integrals of the peaks at $H=0$ for each film are measures of the exposed substrate areas, which are also presented in Table 1 as percentages of the regions scanned by the AFM. At both growth temperatures, one-third to one-half of the substrates were left exposed after *ca.* 100 Å (calculated thicknesses) of CuCl was deposited, but almost 90% of the substrate was covered when the CuCl fluence was nominally doubled. Since islands form during the initial stages of the deposition, the free energy of the bare CaF₂(111) surface must be lower than that of CuCl or of the CuCl/CaF₂(111) interface. From a purely thermodynamic standpoint, the most stable form for the system to take would be a single and nearly spherically shaped island of CuCl on the CaF₂(111) substrate. However the actual films are comprised of many small islands, so the island growth must be limited by the maximum distance that a CuCl molecule can diffuse after landing on the

surface, which is a function of both the substrate temperature and the amount of CuCl already present on the surface.

Our films are evidence that surface diffusion plays a key role in determining the sizes and the shapes of the islands. In the limit of zero surface diffusion range (at 0 K), a thin film deposited from a uniform flux of discrete particles will grow completely stochastically [6] and cover up the substrate fairly rapidly, independent of thermodynamics. At low substrate temperatures, kinetics, not thermodynamics, will control film growth. Raising the temperature increases the diffusion range, thereby relaxing the kinetic constraint and driving the deposition process toward a more thermodynamically favorable situation: for growth by islanding, the areas of the CuCl/CaF₂(111) interfaces and CuCl surfaces will be minimized subject to the constraint of the surface diffusion range. For short diffusion ranges, the islands formed are small and numerous, which is evident from the topographs of the films grown on 80°C substrates in Figs. 1.B1 & 1.B2. As the substrate temperature and thus the diffusion ranges increase, the islands will grow larger, as shown in Figs. 1.A1 & 1.A2.

Reciprocal-space height correlation function. To obtain a more quantitative feeling for the diffusion ranges for our films, we analyzed our quantitative topographical data within the framework of the Shadowing Growth Theory (SGT) [6-9]. Our research group has already employed a modified form of this theory to assist in determining the mechanisms important for the morphology of surfaces formed by sputter-etching [10-11]. The theory compresses the three-dimensional topographical data of a growing film into a two-dimensional mathematical form, the height correlation function, from which we can extract specific kinetic information on the film growth. The starting point of the theory is the Shadowing Growth Equation [6]:

$$\frac{\partial \mathbf{H}(\mathbf{r}, t)}{\partial t} = + J\theta(\mathbf{r}, \{\mathbf{H}\}) - D\nabla^2 \mathbf{H} + \eta(\mathbf{r}, t). \quad (2)$$

The evolution of the real-space height function $\mathbf{H}(\mathbf{r}, t)$, which describes the substrate surface, is governed by three factors during film growth: the flux of the arriving species, surface diffusion,

and noise. In the first term, J is the flux and θ is the exposure angle at the point \mathbf{r} . A key point in the SGT is that the rate of growth at any point on the surface is proportional to how exposed (or how unshadowed) that point is to an incoming isotropic flux. Since our films were grown from a beam source, this term is not strictly applicable to our case, but as we shall see this is not an important point. The second term is the divergence of the surface diffusion current, which describes the effects of surface diffusion: D is proportional to the diffusion constant, or more precisely, $D = D_s \gamma \Omega^2 r / k_B T$, with D_s the surface diffusion constant, Ω the atomic volume, r the number of surface atoms per area, and γ the surface energy per area. The third term in the equation accounts for the shot noise in the arrival of the depositing species and the thermal noise of the substrate. Fourier transforming Eq. 2 converts it into a first order differential equation which can be solved analytically. The resultant reciprocal-space height correlation function is

$$\langle |h(\mathbf{q}, t)|^2 \rangle \propto \frac{J \{ 1 - e^{-[2(Dq^4 + J|q|)]} \}}{D|q|^4 + J|q|}. \quad (3)$$

One particular consequence of the above solution is that at large values of \mathbf{q} , $\langle |h(\mathbf{q}, t)|^2 \rangle$ will be dominated by the $D|q|^4$ term: in fact, as $\mathbf{q} \rightarrow \infty$, the expression simplifies to

$$\langle |h(\mathbf{q}, t)|^2 \rangle \propto \frac{J}{D} |q|^{-4}. \quad (4)$$

When we plot $\langle |h(\mathbf{q}, t)|^2 \rangle$ obtained from experimental data vs. \mathbf{q} on a log-log scale, we should see a straight line with a slope of -4 at large \mathbf{q} if surface diffusion is an important process in the evolution of the film morphology. The calculation of the reciprocal-space height correlation function from an AFM topograph has been described elsewhere [10-11]. It is the Fourier transform of the autocovariance function, defined as

$$G(|\mathbf{r}_2 - \mathbf{r}_1|) = \langle \mathbf{H}(\mathbf{r}_2) \mathbf{H}(\mathbf{r}_1) \rangle - \langle \mathbf{H}(\mathbf{r}) \rangle^2, \quad (5)$$

where $\langle \mathbf{H}(\mathbf{r}) \rangle^2$ is the squared average height of the film.

The reciprocal-space height correlation functions calculated for the four topographs are shown in Fig.2 on a log-log scale. In all four cases, the value of $\langle |h(\mathbf{q}, t)|^2 \rangle$ remains approximately constant for small \mathbf{q} , but starts to drop with a slope of -4 for large \mathbf{q} . The agreement with a -4

slope for large q is extremely good. A slope of precisely -4 was never found in the etching studies because of the influence of redeposition on the morphology of sputtered surfaces [10-11].

From the SGT, the -4 slope we see in our data must be a result of surface diffusion, and the value of q at which the -4 slope begins is the reciprocal of the *surface diffusion length* under the growth conditions of that film, i.e., the average range that a deposited species can diffuse on the substrate. The surface diffusion length ($r_d=2\pi/q_d$) should not be confused with the *diffusion displacement*, which is $\sqrt{4Dt}$, where D is the diffusion constant and t is time. In our case, the diffusion length of a species is dependent not on time, but on the initial energy of the deposited species, on the rate it loses energy to the surface via phonon emission, and on the likelihood of it finding a kink or some other bonding sites. The same quantity of diffusion length has been discussed by Das Sarma, et al.[12], who used it as a parameter in their atomistic numerical simulations of finite size effects in MBE. To our knowledge, no other method can measure the diffusion length of a deposited species on a substrate. This is a remarkably simple, if not unique way to deduce this kinetic parameter. The values of these turn-around points are listed in Table 1 as diffusion lengths r_d . At present, the assignment of their exact positions is somewhat arbitrary, and thus the values of the surface diffusion lengths we have obtained may have a substantial experimental error associated with them, but we have at least tried to be consistent in our assignments. The values calculated for the high fluence films (A2,B2) should approximate the diffusion lengths for CuCl on CuCl, while the values calculated for the low fluence films (A1,B1) should approximate the diffusion lengths for CuCl on CaF₂(111) at the two substrate temperatures. As we expect, the diffusion lengths are substantially longer at the higher temperatures. They are also longer for the thicker films, which means CuCl diffuses farther on itself than on CaF₂; at first this seems incompatible with our observation that CuCl has a lower sticking coefficient on CaF₂ than on itself. A possible explanation is that since CuCl desorbs readily from CaF₂, those molecules that do not quickly find a kink or a defect on the CaF₂ substrate will desorb, leaving behind only CuCl molecules that have landed close to a nucleation center and, in effect, shortening the observed diffusion length.

SUMMARY

We have grown thin films of CuCl on CaF₂(111) substrates at two different substrate temperatures and with two different beam fluences, and then collected quantitative AFM topographs of the resulting surfaces. We found from these topographs that islanding is the dominant growth mechanism for this system. Calculating the height distribution functions for the topographs enabled us to determine the actual volume of the material deposited and the area of the substrate surface left exposed. We then calculated for each film the reciprocal-space height correlation function and compared it to the Shadowing Growth Theory; this analysis provided us with estimates of surface diffusion length of CuCl for the four different growth conditions. They emerged as the most important finding in our studies, since to our knowledge no other method of measuring surface diffusion lengths had existed previously. Our work, though preliminary, has shown that it is possible to extract quantitative kinetic information from AFM topographs. We are hopeful that systematic studies of this type can also be used to extract quantitative *thermodynamic* information and will eventually lead us to a fuller understanding of thin film growth.

Acknowledgments. We acknowledge the Office of Naval Research for financial support, and Prof. R. Bruinsma at the UCLA Department of Physics for providing substantial constructive criticism. WMT is grateful to the Frontier Research Program in RIKEN for financial support during his stay in Japan. The AFM work described in this paper was performed at the Jet Propulsion Laboratory through an agreement with the National Aeronautics and Space Administration.

Figure Captions

Fig.1: AFM topographs of CuCl thin films grown on CaF₂(111) substrates at temperatures and with fluences of 110°C, 60 Å (A1), 110°C, 120 Å (A2), 80°C, 60 Å (B1), and 80°C, 120 Å (B2), as indicated by a thermocouple mounted behind the sample holder and a quartz crystal monitor mounted in close proximity of the growing film. The lateral scale is 50,000 Å by 50,000 Å, and the normal scale has been magnified by a factor of ten to enhance the surface morphologies.

Fig.2: The height distribution functions calculated for the films A1, A2, B1, and B2. The peaks centered at H=0 represent the area of the substrate that was left exposed after the deposition. The widest one has a FWHM of 50 Å, which is small in comparison to a scan area that spans 50,000 Å. Note the scales for the two plots are different.

Fig.3: The reciprocal space height correlation functions $\langle |h(\mathbf{q},t)|^2 \rangle$ for Films A1, A2, B1, and B2. The dashed line denotes a slope of -4, which is in good agreement with the slope of the $\langle |h(\mathbf{q},t)|^2 \rangle$ at large values of \mathbf{q} . The range where the slope is -4 is in real space the length scale where surface diffusion dictates the surface morphology of the growing film. The arrow denotes the point where the slope ceases to be -4, as listed in Table 1 as the diffusion length of the deposited CuCl.

Table 1: Numerical experimental data collected for the CuCl films on CaF₂(111) substrates.

Substrate Temp.	<u>110°C</u>		<u>80°C</u>	
Film	<u>A1</u>	<u>A2</u>	<u>B1</u>	<u>B2</u>
Nominal Thickness (crystal monitor)	60 Å	120 Å	60 Å	120 Å
Root Mean Squared Interface Width	120 Å	210 Å	75 Å	130 Å
Calculated Thickness (height dist. function)	110 Å	390 Å	90 Å	210 Å
Percentage of Exposed Substrate	50%	11%	30%	8%
Diffusion Length r_d	1100 Å	1400 Å	520 Å	570 Å

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Fig 1A1

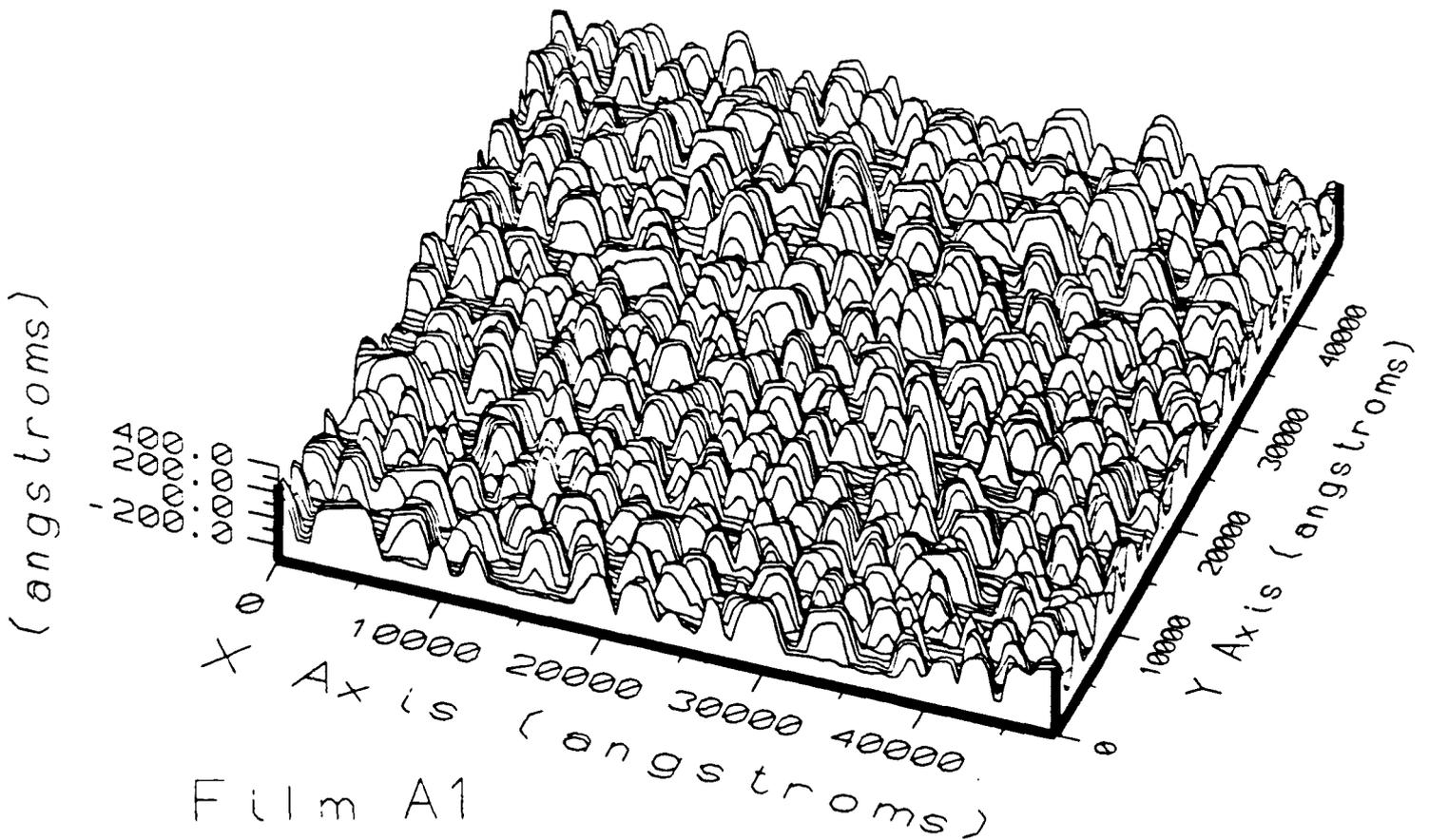


Fig 1.A2

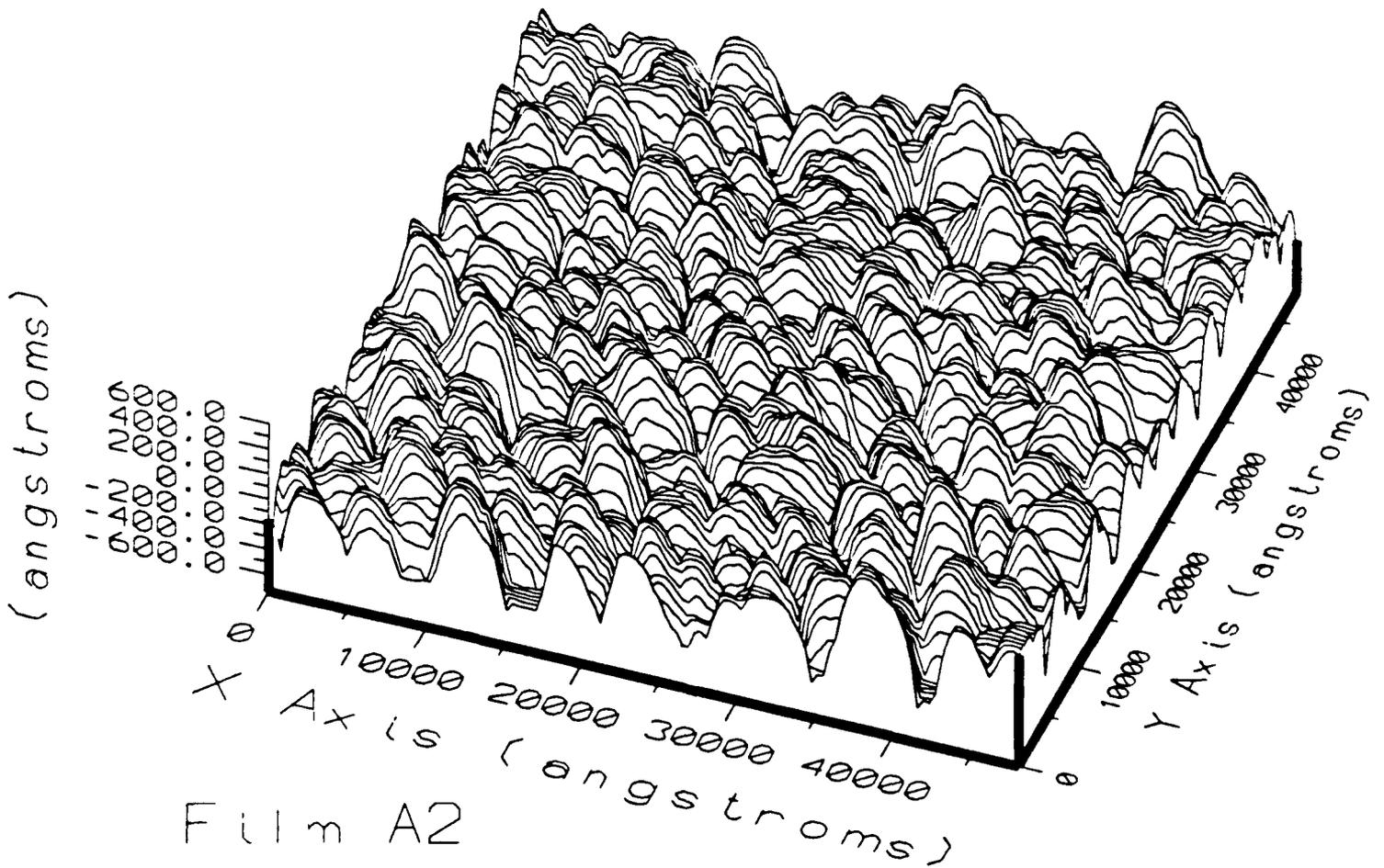
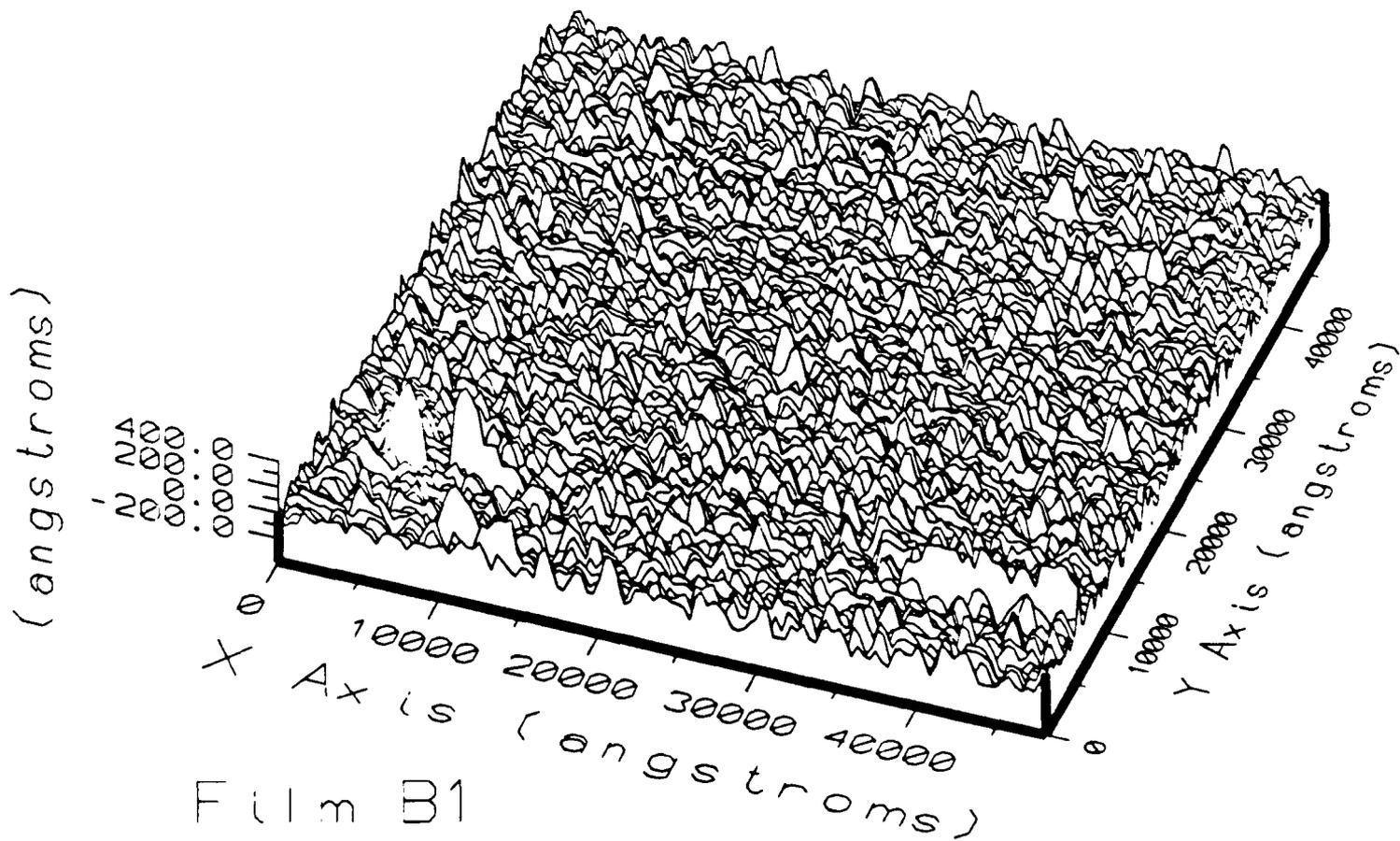


Fig 1.B1



Film B1

Fig 1 B2

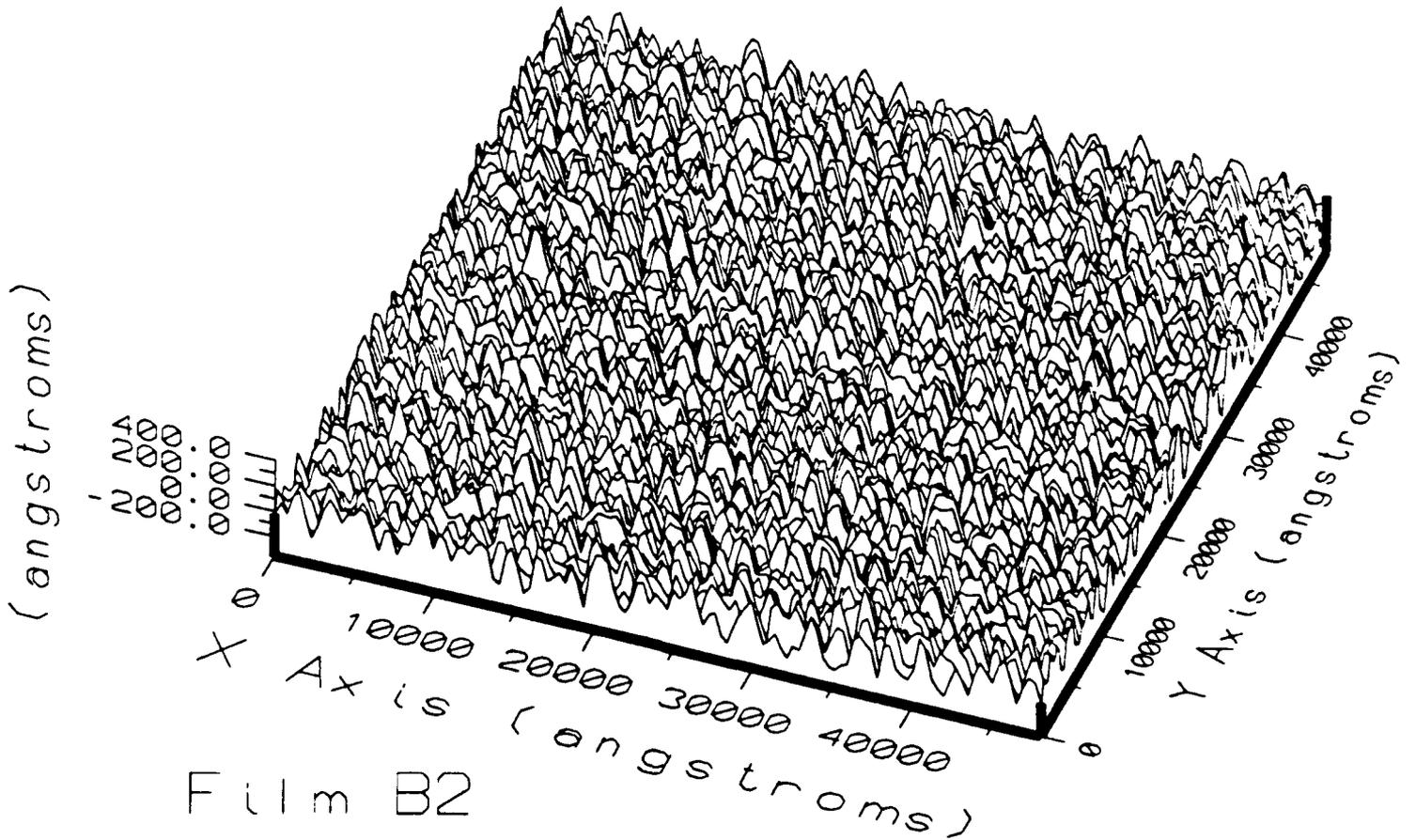


Fig. 2

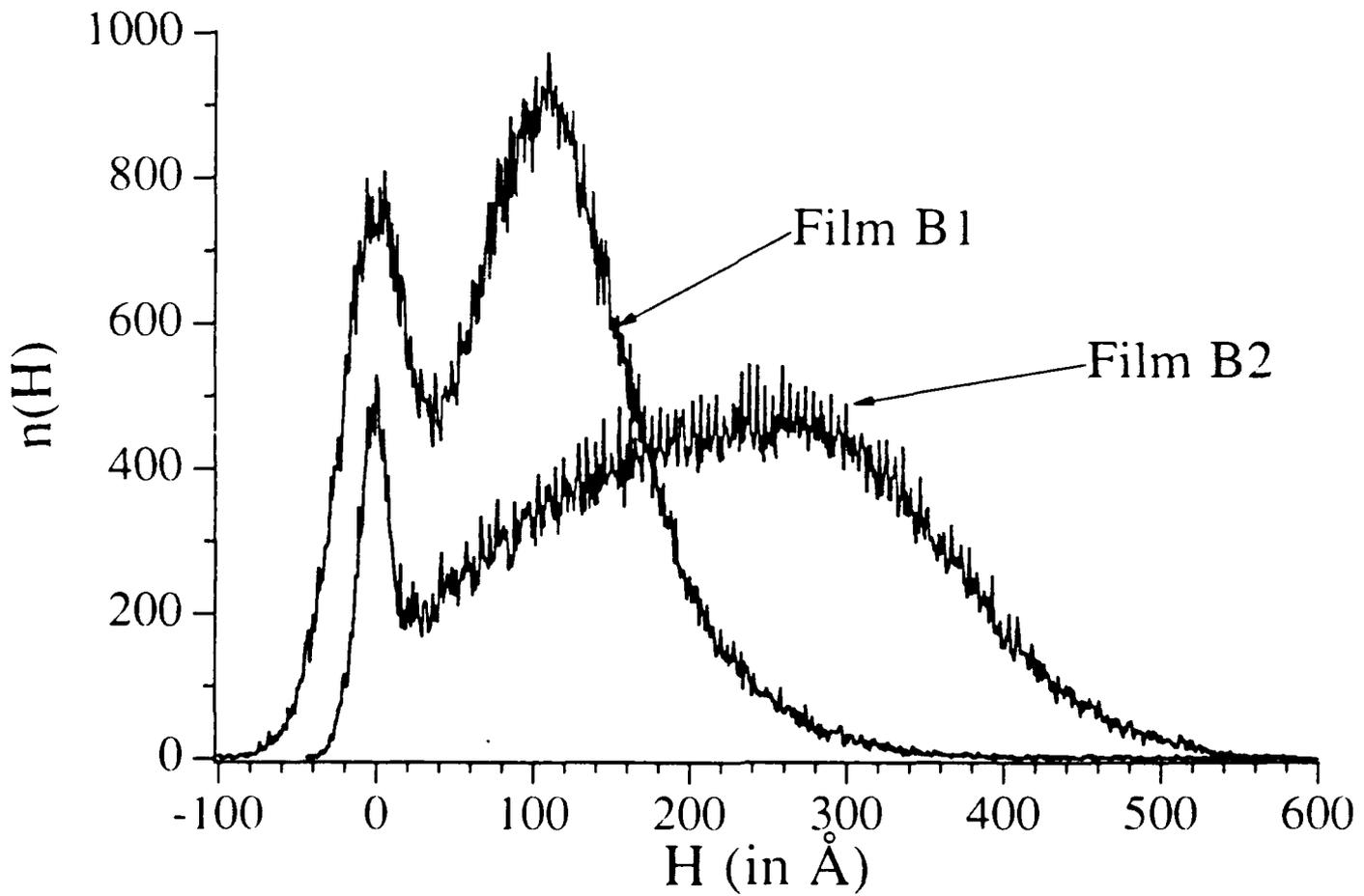
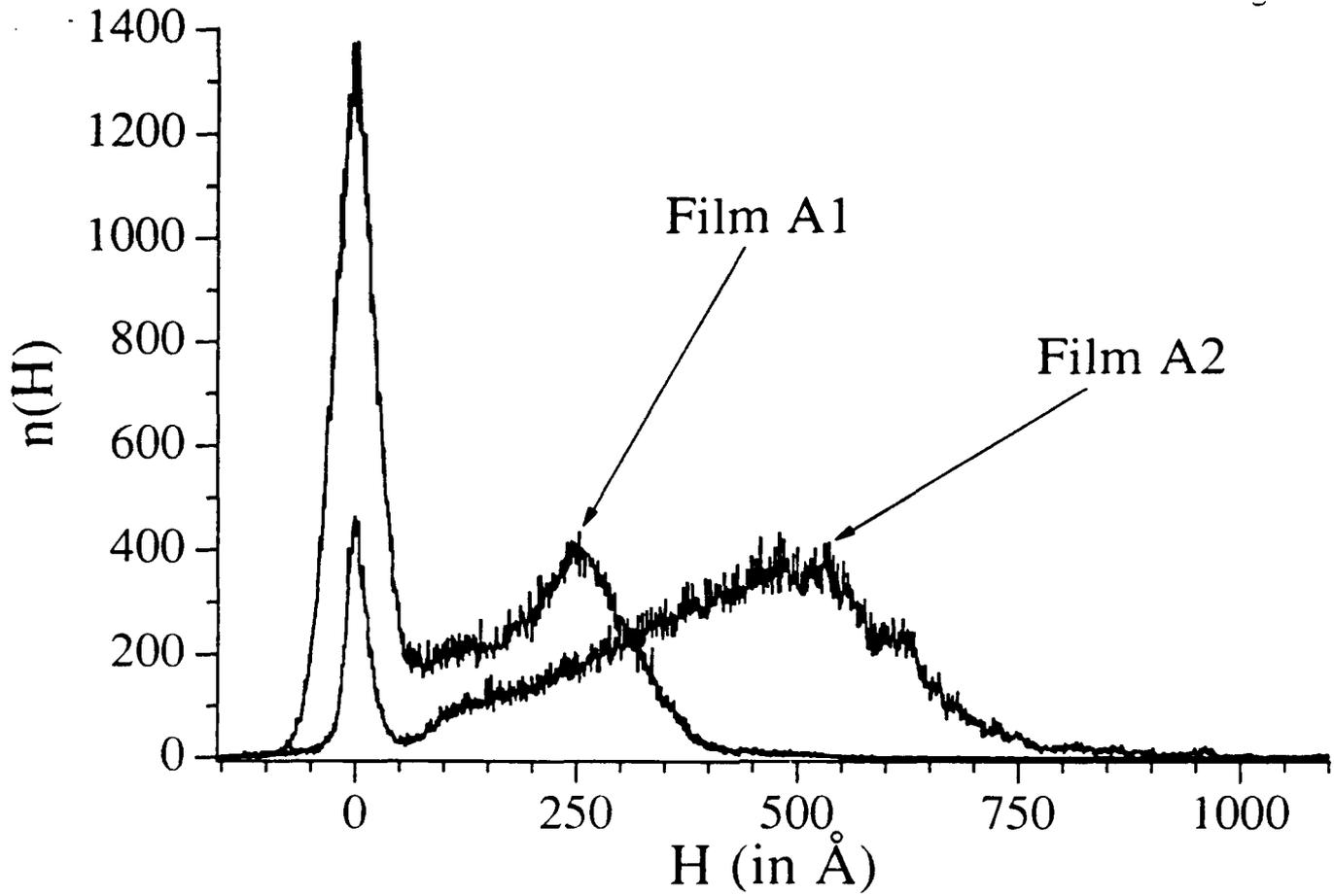


Fig 3

