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IN SITU OBSERVATION OF MONO-MOLECULAR GROWTH STEPS ON AQUEOUS SOLUTION GROWN CRYSTALS AND THE TRANSPORT OF MOLECULES TO THE CRYSTALS

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Direct in situ observation of mono-molecular growth steps on a crystal growing in an aqueous solution became possible. Combination of this method with high resolution Schlieren method or interferometry, growth mechanism of crystals can be investigated directly. Since observation of growth steps on crystals is the most direct and sensitive way for investigating a crystal growth mechanism, it would contribute to reveal fundamental differnces between the growthin space and on earth. The method was recently extended to in situ observation of the growth processes at high temperatures (1800K).

1. INTRODUCTION

Crystal growth takes place when molecules are integrated to a crystal at the surface via transport of molecules from the bulk solution to the crystal surface. It is therefore necessary to investigate both transport phenomena of molecules by, for instance, diffusion and the integration of molecules at the surface, if one wants to understand the crystal growth mechanism from a fundamental point of view. The former investigation has been performed even before the beginning of this century, leading to development of the Fick's law for the interpretation of growth rate and theories on morphological stability of a crystal. This kind of investigation has been carried out in some space experiments, and, of course, on earth. However up to now there is no plan to investigate crystal growth kinetics at the surface in space. It is very important to investigate the movement of molecular growth steps in space in absence of hydrodynamic perturbations because the movement of the steps and the shape of the steps reflect the growth mechanism in a very sensitive way.

It migh have been considered to be impossible or very difficult to observe such thin steps with the height of less than 1nm during the growth of crystals. However thanks to recent developments on in situ surface observation techniques, one can see the moving mono-molecular growth steps on a TV monitor. It is here proposed to employ in situ observation system for the investigation of crystal growth mechanism in space with the combination of Schlieren method or interferometry to visualize the transport phenomena of molecules to the surface. On earth crystal growth is enhanced due to the presence of convection flows near the surface, otherwise good mixture of the solution near the surface cannot be obtained, leading to unstable growth or inhomogeneous crystals. It is also expected that the absence of convection would lead to a complex growth behavior especially at very low supersaturations because presence of small concentrations of impurity would easily stop the movement of growth steps in space. This kind of complex behavior cannot be predicted exactly from theories. Therefore it would be fruitful to compare the surface of crystals grown in space and on earth by sensitive in situ surface observation techniques.

2. BRIEF HISTORY ON SURFACE OBSERVATION

The growth mechanism of a crystal in an aqueous solution is one of the topics in which scientist are now interested in. Already in 1930 scientist theoretically knew that crystal growth proceeds by pilling up of molecular growth steps which laterally move on a surface. An important theory was put forward in 1949 by Frank [1], namely the spiral growth theory. After the development of the theory, the first spiral was observed in 1951 on a natural beryl crystal and many examples have been reported thereafter. However it was not easy to observe mono-molecular growth steps on crystals like NaCl or K-Alum grown from an aqueous solution. This is because the surface cannot be easily separated from the mother solution without destroying the original surface pattern.

Another experimental method has been applied to verify the proposed spiral growth theory. The growth rate of a crystal was measured at very low supersaturation (less than 1%). This relation is determined by the growth mechanisms. Bennema [2] measured the growth rate of crystals versus supersaturation in aqueous solution and showed that this could be explaned by spiral growth theory.

In 1972 observation of spirals was reported on NaCl grown from an aqueous solution [3] by applying suitable surface treatments and very sensitive optical phase contrast microscopy. Up to now many crystals were found to grow by a spiral growth mechanism through careful surface observation [4]. However it was found that both experimental results were not always consistent. So a new experimental method was required. It was Tsukamoto who showed that direct in situ observation of mono-molecular growth steps on a crystal in a well controlled queous solution is possible and thus coupling the in situ surface observation with kinetic measurements, like growth rate measurements enabled us not only to investigate actual growth mechanisms more precisely but also to find new phenomena which have not been taken into account for the interpretation of crystal growth processes [5].

This in situ observation was started to observe a crystal surface but later high resolution Schlieren method and Mach-Zehender interferometry were added to the system, so that one can see how molecules (growth units) are trasported to the crystal surface. This was further developed recently so that one can employ this in situ observation method to the growth of crystals even at high temperatures, $<1800K$, which is now being employed for some oxide crystals grown from high temperature solutions or melts.

In this paper only the principle of the observatin and some of the results will be shown. It may be noted that proto-types of the in situ observation system for both aqueous solution growth and high temperature growth for GAS experiments are already constructed, which show even better resolution than the system which we are now employing in our laboratory, though the size and the weight are much smaller.

3. OBSERVATION METHOD

In order to obtain the image of growth steps on a crystal growing in an aqueous solution, either phase contrast microscopy or differential interference contrast microscopy is employed. Both types of microscopy can reveal very thin growth steps of a few Å. Depending upon the purpose, either transmission or reflection type microscopy can be chosen.

By these microscopies the invisible phase difference arising from the adjacent steps with different level can be converted into visible intensity difference. The optical images are stored on video tapes after some image processings, fig.1 [5,6].

Although these microscopes have been known to be powerful for surface observations, a serous problem arises when one wants to carry out in situ observations, namely the sharp increase of optical aberration due to the fact that the surface of a crystal is observed through a thick solution and glass windows. Our high resolution in situ observation was derived from the success in suppresing large optical aberration by designing new optical systems. The importance of suppressing optical aberration is as an example shown in fig.2, in which the thickness of the solution is 10mm. One cannot see even the shape of the small crystals attached on the side faces of the seed crystal if optical aberration appears. The same principle is applied to the other optics, such as Schlieren method or laser scattering methods.

4. PRESENT PROBLEMS

Our in situ observation system for aqueous solution growth has been applied to solve the following problems, for instance, fig.3.

(1) growth rate of crystals grown in aqueous solution, which is not proportional to the concentration gradient towards the surface

(2) relation between the hydrodynamics of the solution just near the surface and the growth rate or the perfection of the crystal

(3) structure of solution with the combination of laser scattering techniques, in which clustering of molecules is already found in supersaturated solution before nucleation

(4) development of a high density liquid layer (less than 100 micron thick) in a diffusion boundary layer (about 400 micron thick), which is closely related to the birth of secondary nuclei in the solution

(5) the relation between the structure of a solution and the structure or perfection of the crystal

5. CONCLUSION

In situ observation, especially surface observation, is very powerful method to detect slight change of growth mechanism or growth conditions in a short time and therefore is concluded to be very useful for the growth experiments in microgravity, fig.4 and fig.5.

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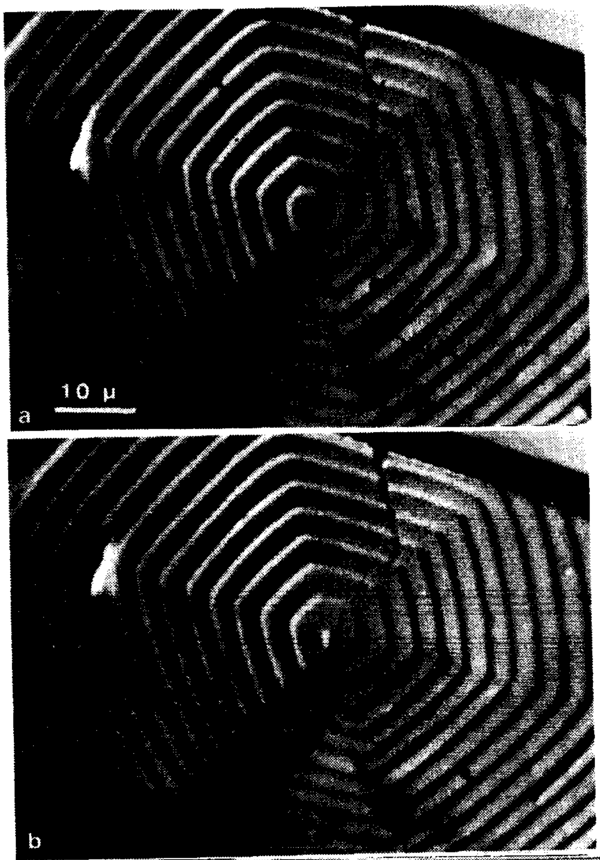
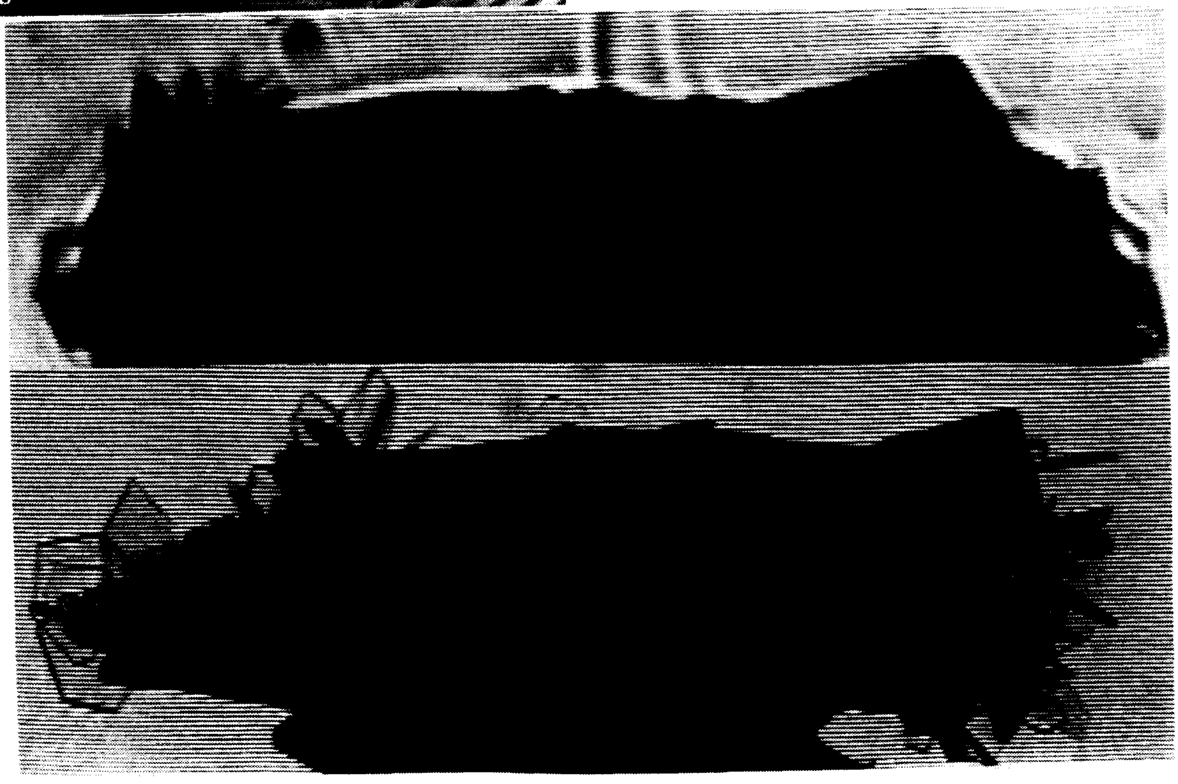


fig.1

Spiral growth steps on CdI_2, taken by differential interference contrast microscopy, photographed from a TV monitor, in situ

fig.2

Improvement of optical images by suppressing the optical aberration due to the thickness of the solution (10mm) in the optical path



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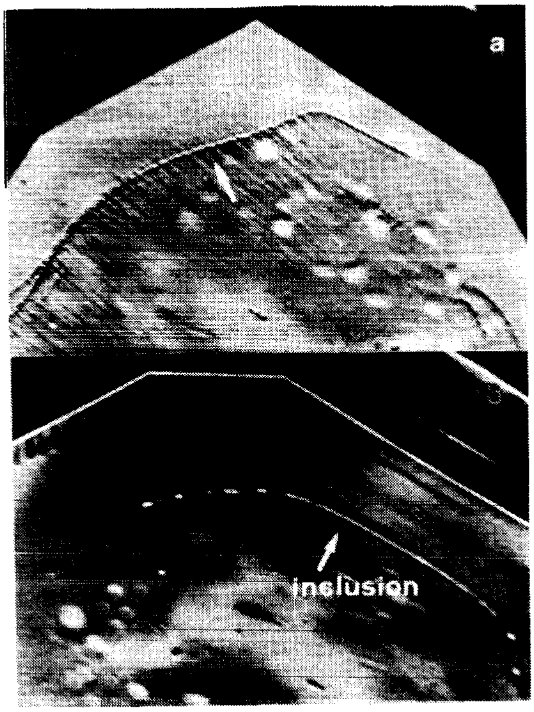

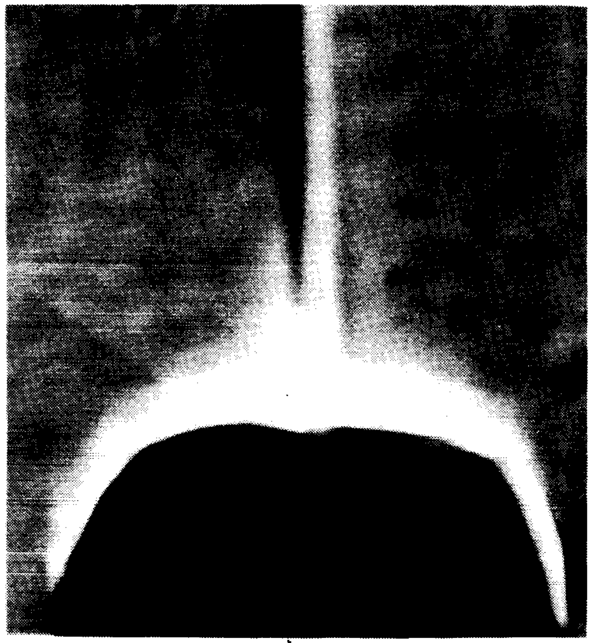

(b)

fig.3 Inclusion trap due to the development of a convection plum, when the supersaturation is above 0.5%, (a) surface micrograph and (b) Schlieren image

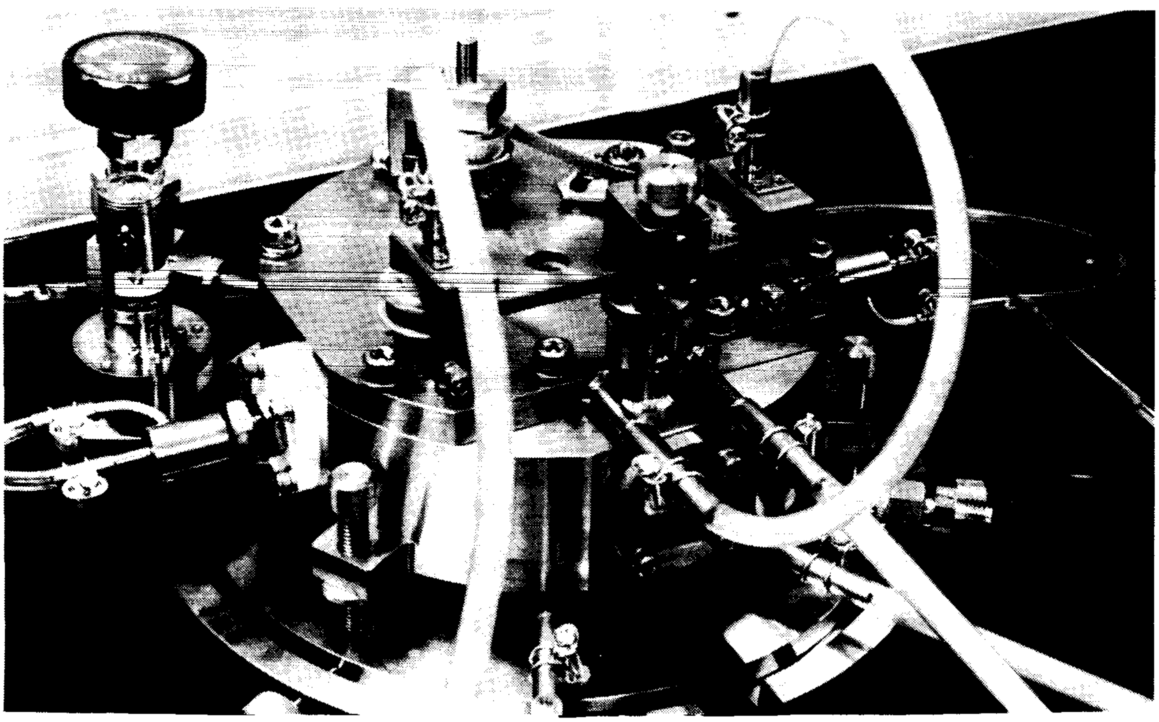

fig.4 (a)

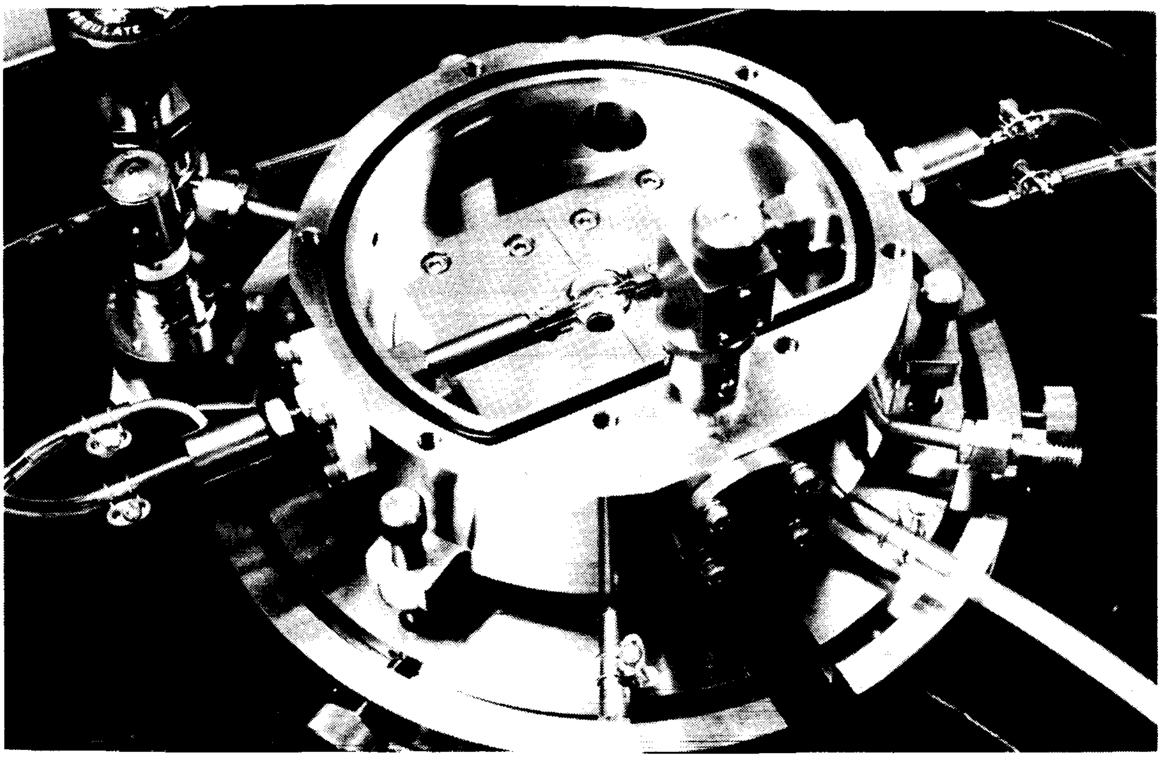

fig.4 Proto-type growth cell at high temperature (1800K) for in situ observation, (a) outside view and (b) the inside, 15cm in diameter

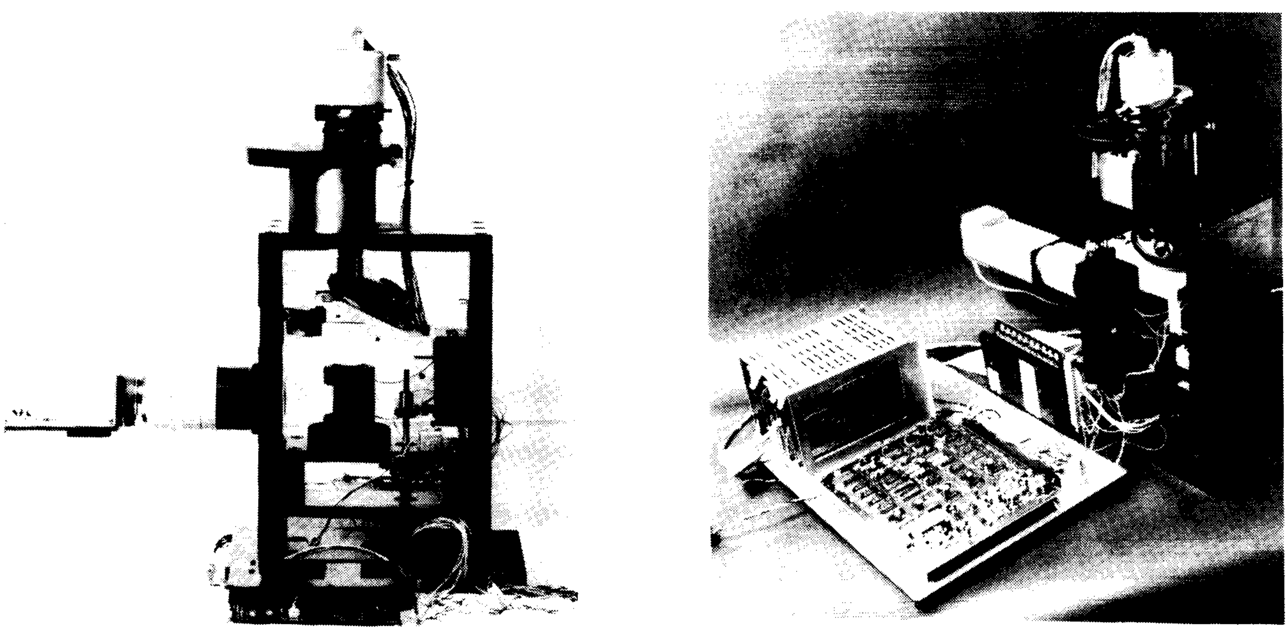

fig.5 Proto-type microscope in microgravity, by which one can observe growth steps with mono-molecular height and automatically measure the growth rate of a crystal