Bharathidasan University
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Programme: M. Sc. Physics

Course Title : Crystal Growth Methods and Characterization

Code : 22PH443

Unit V : Chemical Etching

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Chemical Etching

INTRODUCTION

When a crystal is subjected to any physical or chemical process, the weakly bound growth units *dislocations* may dissociate themselves from the crystal leaving a *shallow etch pit*. **This phenomenon is known as etching**.

These shallow etch pits can be observed on the *surface of the crystal* by adopting the dissolution techniques.

Etching gives rise to various *types of geometrical features* on a crystal surface.

As single crystals are *anisotropic*, the rate of attack by the etchant (solvent) on the crystal surface is also anisotropic.

This anisotropy produces *conical depressions* with regular geometrical outline on crystal surface. **This is known as etch pits, etch marks or etch figures**.

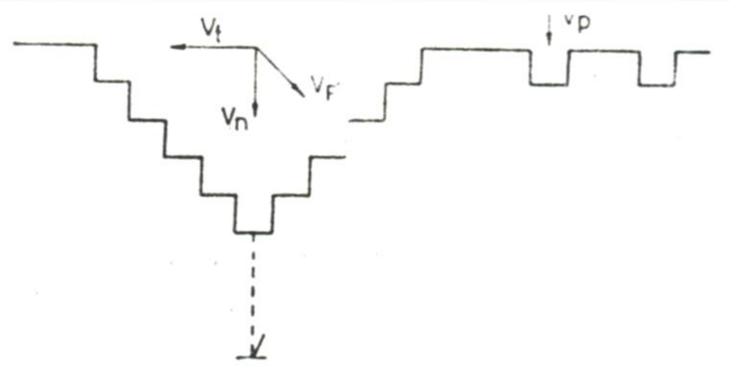
ETCHING PIT FORMATION

The necessary condition for the formation of visible etch pits is the proper ratio of the three dissolution rates.

The first one, the normal etch rate V_n along the dislocation line, is *directed normal to the surface*.

The *tangential or lateral etch rate* V_t describes the rate of spreading up of elementary steps along the surface.

Finally, the rate V_p describes the *dissolution (or polishing)* of the surface in areas free from dislocations. The rate is also directed normal to the surface.



The different etch rates involved in the formation of an etch pit at a dislocation site

MORPHOLOGY OF ETCH PITS

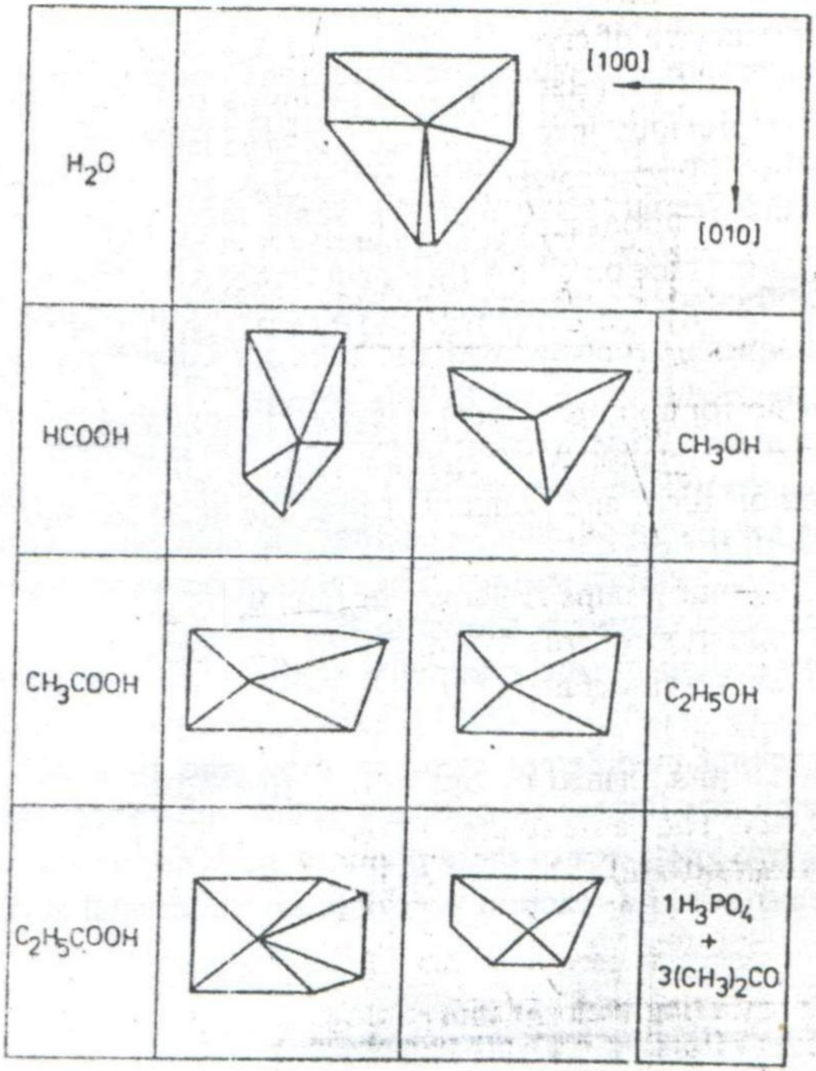
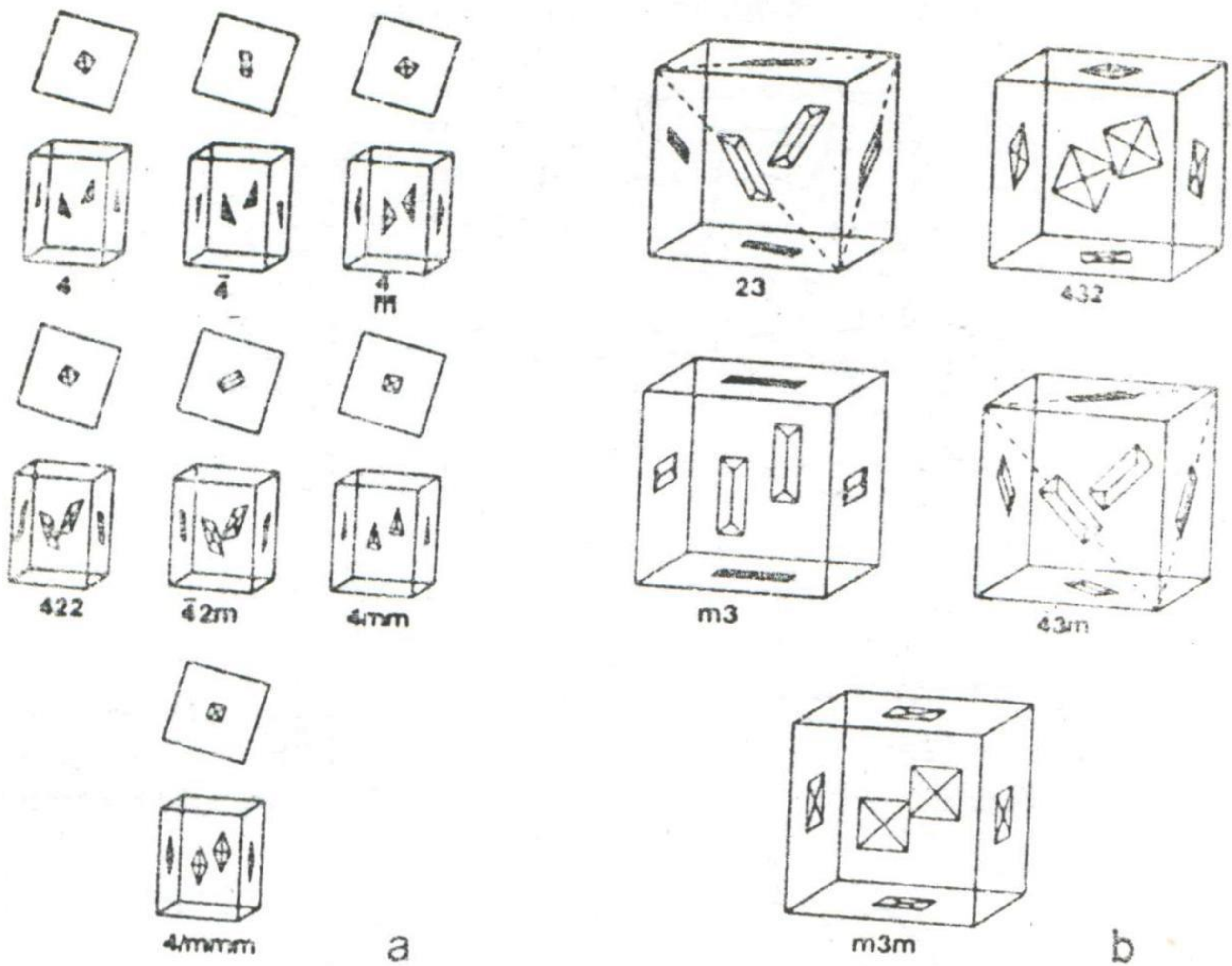


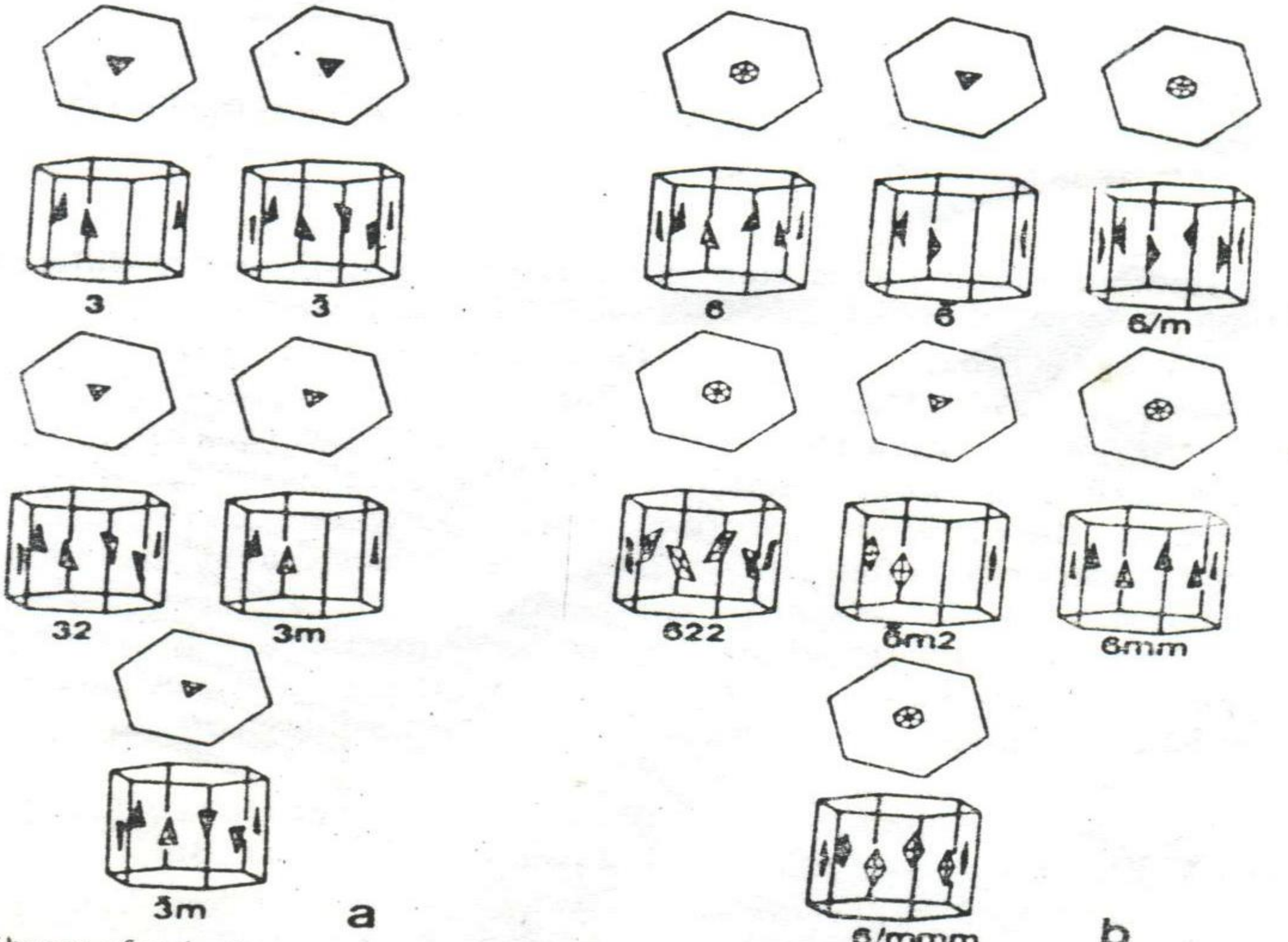
Fig. 9.4. Morphology of dislocation etch pits observed on the (001) face of triclinic $K_2Cr_2O_7$ crystals (Sangwal and Szurgot 1982).

MORPHOLOGY OF ETCH PITS



g. 9.3. Shapes of etch pits on crystals with (a) tetragonal, and (b) cubic point groups (Buerger 1956).

MORPHOLOGY OF ETCH PITS



?2. Shapes of etch pits on crystals with (a) trigonal, and (b) hexagonal point groups (Buerger 1956).

MORPHOLOGY OF ETCH PITS

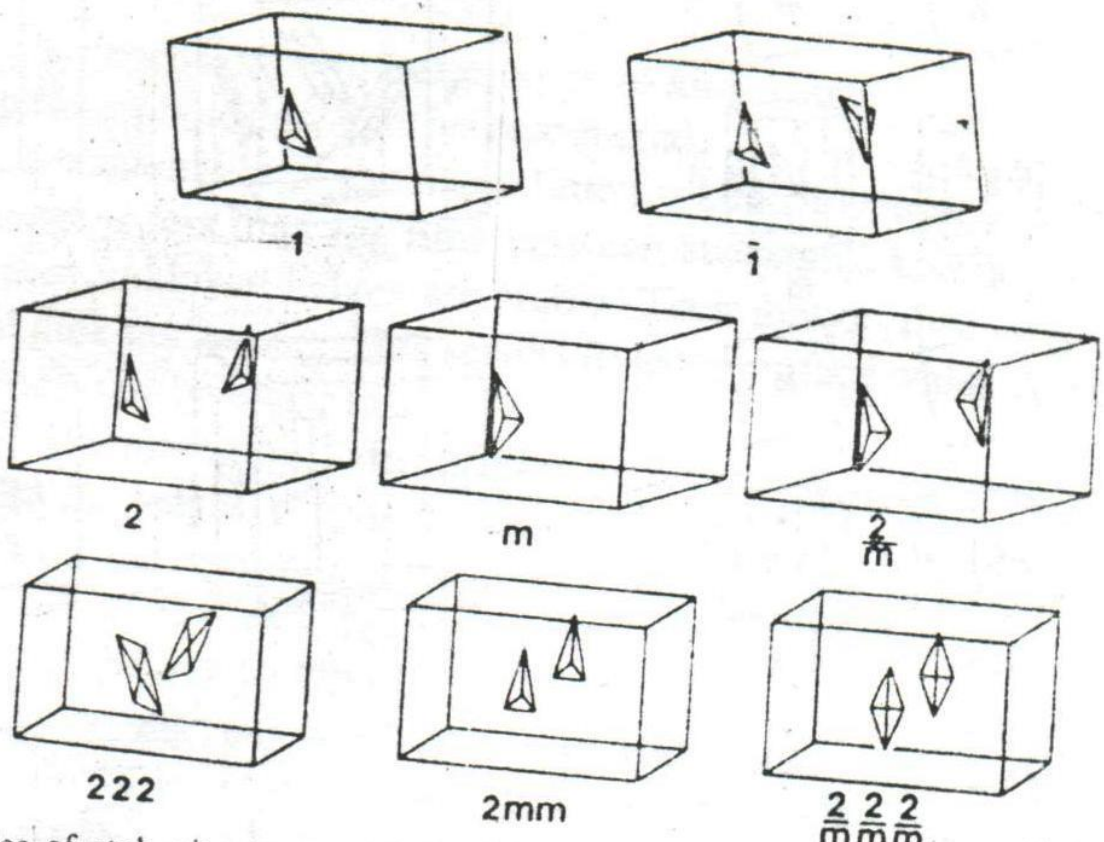


Fig. 1. Shapes of etch pits on crystals having triclinic, monoclinic, and orthorhombic groups (Buerger 1956).

METHODS OF ETCHING

There are many ways of etching preferential dissolution on a crystal surface. They are

- **Chemical etching**
- **Thermal etching**
- **Ionic etching**
- **Electrolytic etching and**
- **Dehydration etching**

Among these methods chemical etching method is discussed below.

CHEMICAL ETCHING

Chemical etching includes major portion of research in etching and substantial work on different crystals is now available in literature.

Chemical etching produces a few or all of the following etch features on a crystal surface:

- etch spirals
- etch pits, terraced, flat bottomed and point bottomed
- linear etch rows
- polygonised etch figures
- tunnels and dentritic etch features
- shallow pits, etch hillocks

CHEMICAL ETCHING

Properties of crystal depend on the quality of the crystal which may affect the properties of

light absorption,
scattering,
refractive index,
chemical homogeneity,
mechanical strength and
thermal stress.

Chemical etching is one of the methods to study the micro-structural imperfections in the as-grown crystals.

Chemical etching process can be performed using different etchants which give specific shapes of etch pits.

EXPERIMENTAL PROCEDURE

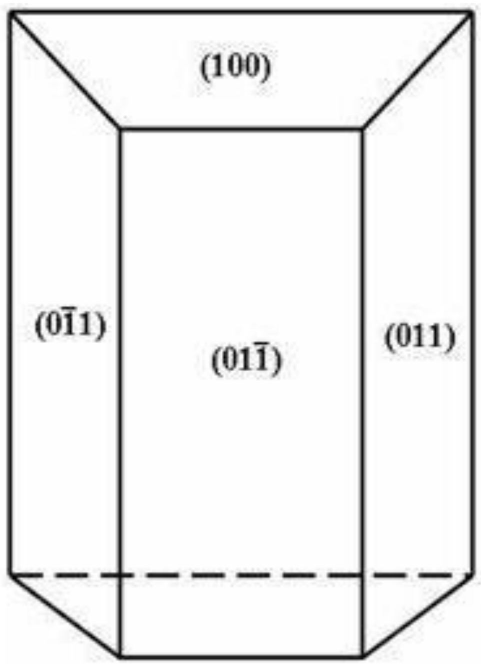
The rate of reaction of an etchant with a solid surface depends distinctly on the crystallographic orientation of the reacting surfaces.

<100> and <011> orientations of grown single crystals were subjected to etching using two different etchant (deionized water and formic acid) for two different etching time (20 s and 60 s).

The crystal face was dipped in the etchant for the required etching time and then wiped with dry filter paper.

The observed etch patterns were photographed with an optical microscope.

EXPERIMENTAL PROCEDURE

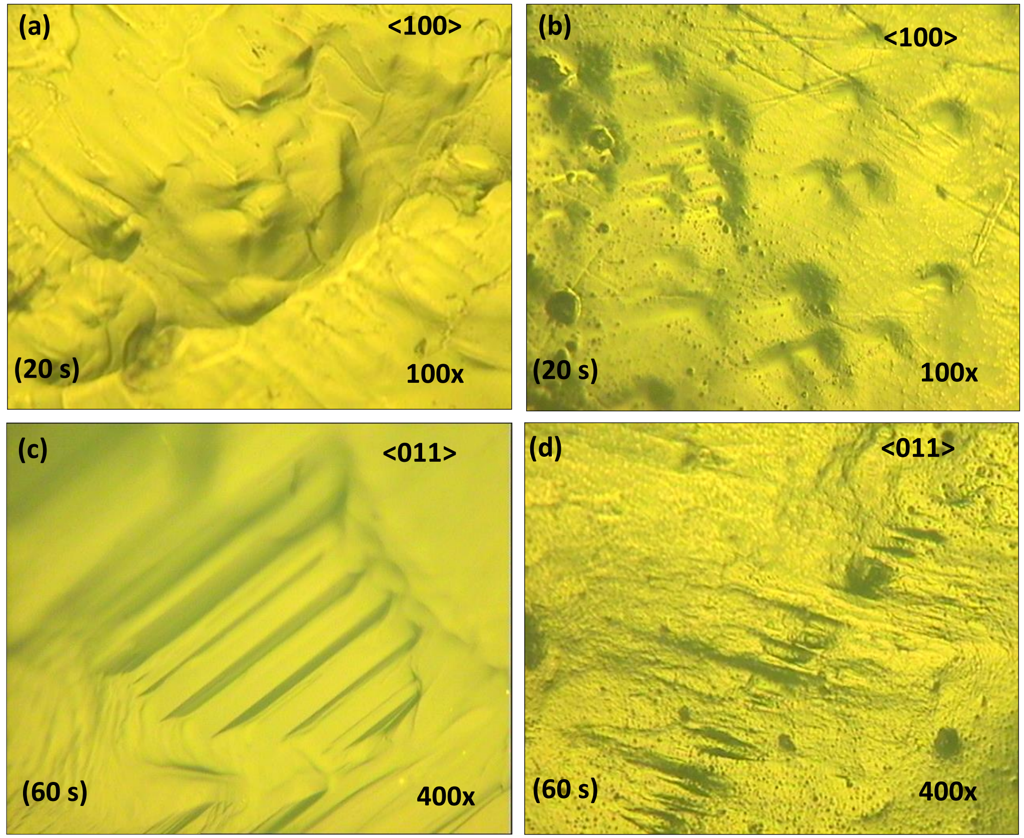


Etchant - water

Etching time - 60s

Optical microscope – view the image

ETCH PATTERNS



Etch patterns of L-LMHCl crystal etched with (a, c) deionized water and (b, d) Formic acid etchants

EXPERIMENTAL RESULTS

Fig.a shows the pyramidal shaped etch hillocks obtained from etching the <100> orientation of crystal using deionized water etchant for etching time of 20 s.

Formation of these *hillocks is due to incorporation of impurities during the crystal growth* which introduced strain in the crystal lattice.

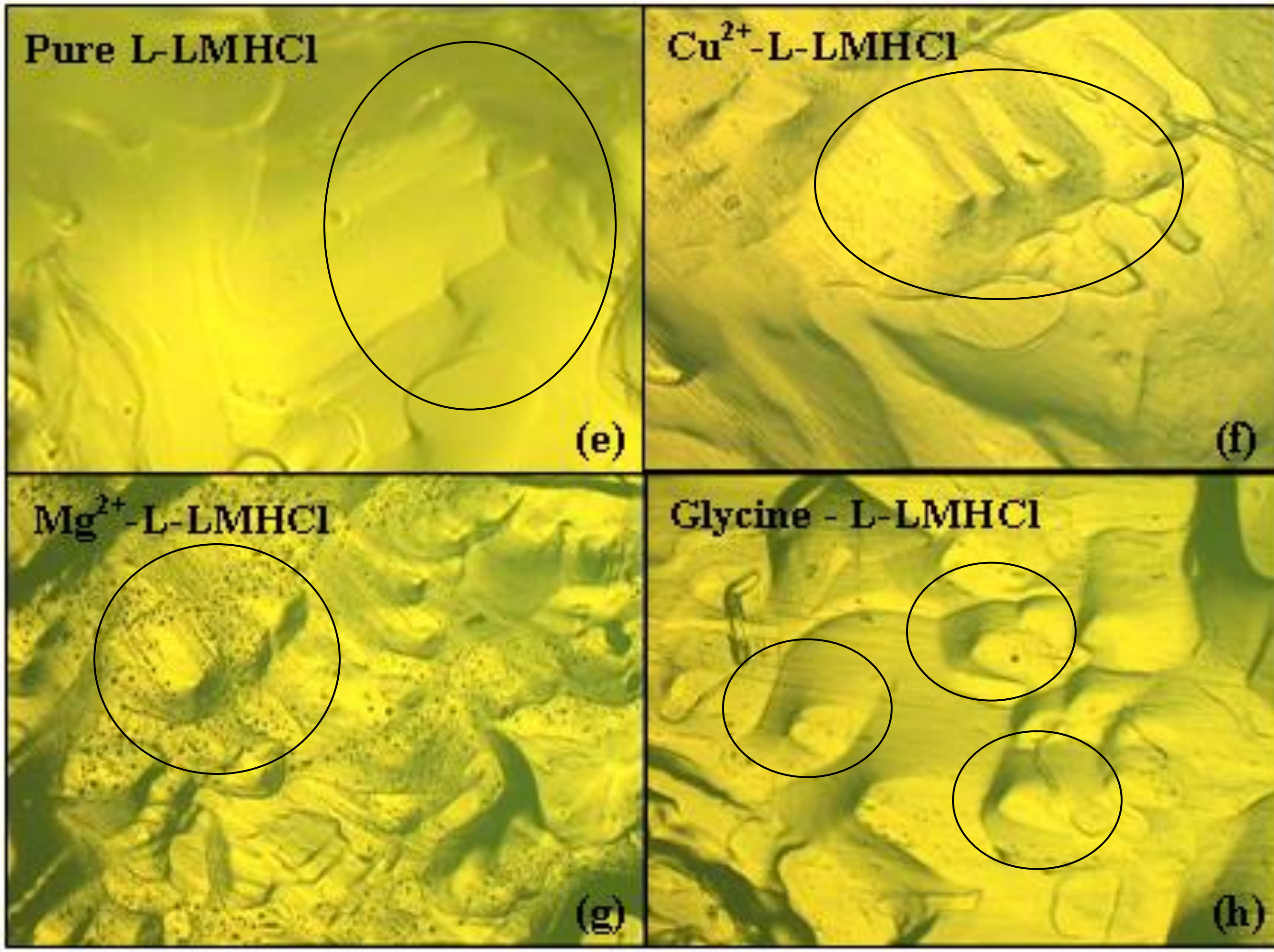
When formic acid was used as etchant, the well defined and *regular etch hillocks were formed* (Fig. b). Fig. c shows the rectangular growth hillocks when the <011> orientation of the crystal was etched with deionized water for 60 s.

EXPERIMENTAL RESULTS

The observed *rectangular growth hillocks reveal the emergent points of dislocations*. When the surface of <011> orientation was etched with formic acid for 60 s the etch pits are not observed (Fig. d).

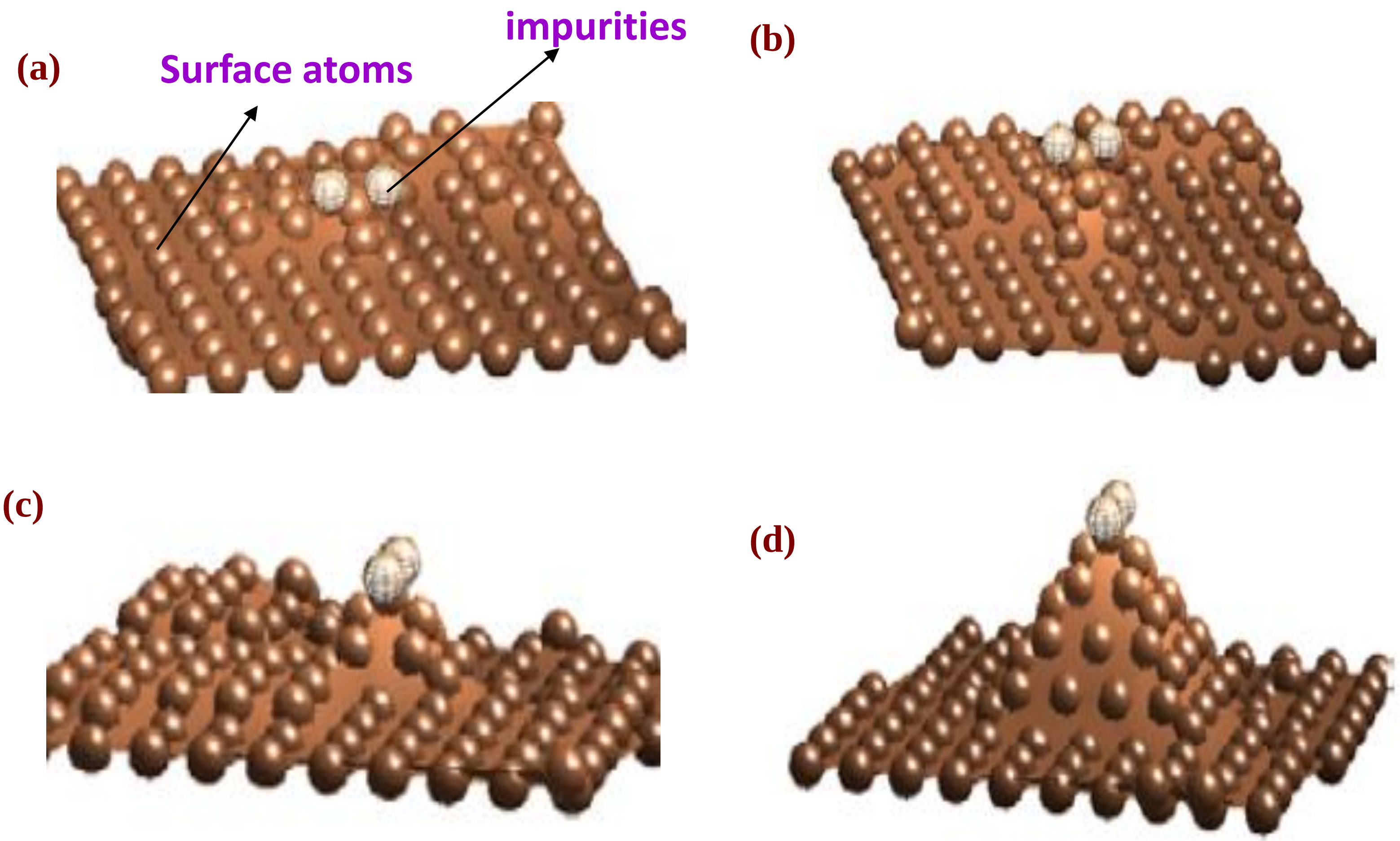
From the above results it was observed that formic acid could produce well developed etch patterns on <100> orientation compared to the corresponding etch patterns produced by deionized water etchant. But in the case of <011> orientation deionized water seems to be the suitable solvent to produce etch pattern.

ETCHING STUDIES ON (100) PLANE



Surface micromorphology patterns of pure and doped L-LMHCl single crystals along <100> orientation

Formation of Pyramidal Etch Patterns



The hillocks are nucleated in order to stabilize the two initial apex atoms

ETCHING STUDIES ON SULPHAMIC ACID CRYSTALS

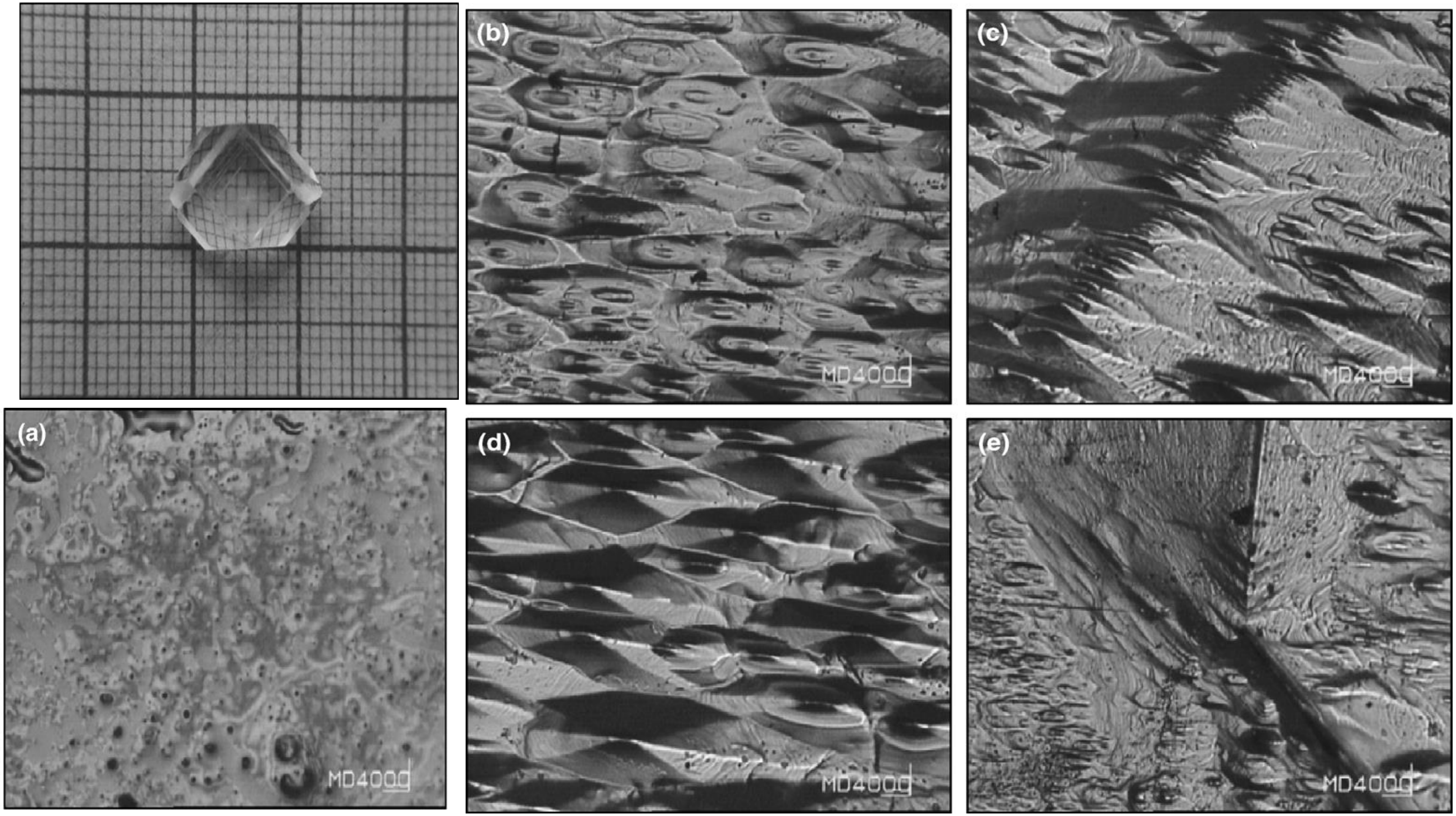
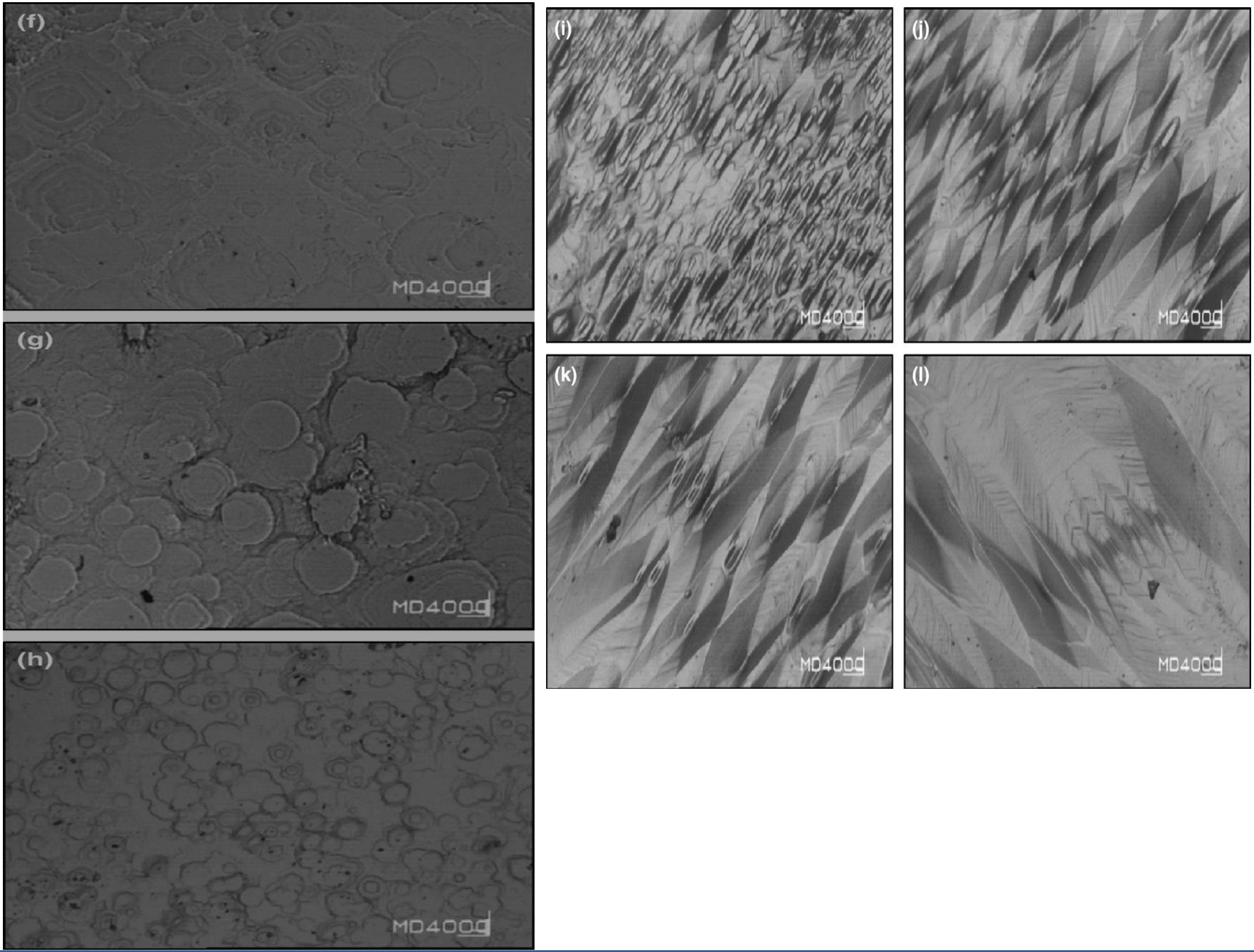


Fig. 3. (a) Surface of as grown SA crystal. (b), (c), (d) and (e) Surfaces of SA crystal etched by water for 5 s, 30 s, 1 min and 5 min, respectively. (f), (g) and (h) Surfaces of SA crystal etched by ethanol for 5 s, 10 s and 30 s, respectively and (i) , (j), (k) and (l) surface of SA crystal etched by HCl for 3 s, 5 s, 10 s and 15 s, respectively [magnification 400×].


(f)
(g)
(h)
(i)
(j)
(k)
(l)

BOOKS FOR REFERENCE

1. K. Sangwal, Elementary Crystal Growth (Edited) (SAAN Publishers, Lublin, 1994).

2. R. Rodriguez-Clemente and C. Paorici, Crystalline Materials: Growth and Characterization (Etd.) (Trans Tech Publications Ltd, Switzerland, 1991).