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Discontinuities at the interface and adhesion

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Abstract

An adhesive bond does not necessarily fail at its "weakest link". The loading mode, the thickness of the adherends and adhesive layer, the presence of localised flaws, and of residual stress state within the adhesive layer can all affect the failure strength and energy of an adhesive bond. This means that very similar adhesive bonds may exhibit different failure energies and different loci of failure. This paper reviews some examples from the literature where the introduction of discontinuities at the interface also leads to differences in failure energy and locus of failure. The influence in this way of microporous and microfibrinous surface features in anthropogenic adhesive bonds are well-established. More recently, it has been recognised that analogous effects occur in some examples of adhesion in the natural world. The remarkable climbing ability of the gecko depends of a fine state of subdivision at the interface between the animal's foot and the substrate. Studies of natural adhesion has stimulated the development of biomimetic adhesive systems, for example using photoresist technology to produce microfibrinous and microporous surfaces.

Keywords: biological adhesive; biomimesis; microfibrinous; microporous; interfacial stress; locus of failure.

1 INTRODUCTION

In any adhesive system it is of interest to understand the conditions under which failure will occur. In principle failure may be adhesive at the adhesive-substrate interface, cohesive within the adhesive or substrate, or perhaps some mixture of these different failure modes. There is a temptation to suppose that failure will occur wherever the system is "weakest". Adhesive failure will result from weak interfacial forces; cohesive failure from weakness in one of the phases present and perhaps failure close to the interface from the presence of a weak boundary layer.

In practice, the situation is more subtle than this. According to the Griffith-Griffith theory of fracture, the fracture stress, σ_f , of a material is given by

$$\sigma_f = k(EG/l)^{1/2} \quad (1)$$

where k is a constant, l is the length of the critical crack which leads to fracture and E is the modulus and G the fracture energy. Good [1] used this simple mathematical framework to discuss the fracture to a joint comprising a bond between two phases. It lends itself to a clear discussion of the factors which control locus of failure.

Within the adhesive joint, E and G , as Good pointed out, are semi-local properties. Fracture will occur where the term EG/l is lowest, whether at or near the interface or within one of the bulk phases. Factors which alter E or G or l locally within the joint may alter its strength and locus of failure. Good showed that cohesive failure close to an interface may occur as a result for example if E increases, but G decreases, passing from adhesive to substrate, and may have nothing to do with weak boundary layers.

This argument is, of course, essentially a fracture mechanics argument, albeit applied to a very simple system. Among David Dillard's contributions to our understanding of adhesion is his work on the application of fracture mechanics to much more complicated situations. Explicitly Dillard raises the question "Does an adhesive bond fail at the weakest link?" [2], and shows both theoretically and practically, that quite different loci of failure can be obtained with identical joints, depending on the loading conditions. As Dillard says "The crack path of a growing crack is determined by a number of factors in addition to the relative strength or fracture energy of the adhesive layer and the interfaces or

interphases; these factors include the loading mode, the thickness of the adherends and adhesive layer, the moduli and ductility of the adherends and adhesive, the presence of localised flaws, and the residual stress state within the adhesive layer" [2]. Figure 1 [2] illustrated four different failure modes produced in identical specimens of aluminium sheets bonded with the same epoxy adhesive. The different failure modes are the result of different loading conditions. A shear stress will tend to drive the crack to one interface; a tensile stress within the bond plane can destabilise growing cracks, causing them to oscillate within the adhesive layer or from substrate to substrate. A fuller development of these ideas is to be found in Chen & Dillard's article [3].

Thus the work of Dillard and others has shown quite clearly that different loci of failure and different failure loads can be obtained from similar, or even identical, adhesive bonds, depending on the stress state. The stresses within a bond can be changed by different loading régimes and by changing geometric factors such as substrate and adhesive thickness. The stress state can also be altered by introducing discontinuities at the interface. In anthropogenic adhesion, use of microporous or microfibrinous interfaces can markedly alter the "strength" of an adhesive bond, even where the physical and chemical properties are not significantly changed. The natural world provides some spectacular examples of adhesion which in their versatility and reversibility out-perform anything which human ingenuity can yet achieve. Careful examination has shown that a number of these natural examples rely for their effectiveness on fine subdivision at the surface of contact.

The purpose of this paper is to review some examples of discontinuities at the interface and to examine their effect on adhesion, with reference both to anthropogenic and natural adhesion.

2. MICROPOROUS SURFACES

Ever since the resurrection of the mechanical theory of adhesion in the later 1960s [4-9], it has been recognised that microporous surfaces often provide effective substrates for adhesive bonding. A classic example of such surfaces is provided by porous oxide films produced on aluminium by anodising in an aggressive electrolyte, such as sulphuric or phosphoric acids. The pore structure is shown schematically in Figure 2. Although phosphoric acid anodising (PAA) has been used as a pretreatment in the aircraft industry for years [9], the development of new microporous morphologies by this method is still an area of active research [10]. PAA generally provides durable bonds of good strength. In aviation it is the durability which is of critical importance, but here we will be more concerned with *why* the adhesion is good.

Epoxides, and some other structural adhesives, will bond adequately to aluminium with a range of surface treatments; it is the bond durability in an aqueous environment which demonstrates the superiority of those which produce microporous surfaces. It will be easier to isolate the effect of the microporous surface *per se* by considering an adhesive-substrate combination where the presence of pores makes a large difference to the adhesion obtained. Therefore the adhesion of polyethylene to aluminium will be considered.

Table 1 shows results for the peel strength of low density polyethylene applied as a model hot melt adhesive to aluminium. With a relatively smooth degreased aluminium surface poor adhesion is obtained, but when the aluminium is anodised to give a porous oxide film, much higher peel energies are obtained [5].

3. MICROFIBROUS SURFACES

A similar effect is obtained with microfibrinous surfaces on metals. Table 1 also shows low peel energies for polyethylene peeled from a polished copper surface and much higher peel energies for a similar substrate oxidised to give an array of microfibrines of copper (II) oxide [11] similar to that shown in Figure 3. Similar effects have been demonstrated with microfibrinous surfaces on zinc and steel.

The failure mode associated with the results shown in Table 1 is characteristically different for the smooth, compared with the rough surfaces. With smooth surfaces failure is at, or close to the interface with little or no plastic deformation of the polyethylene evident by examination in the scanning electron microscope. By contrast, the microporous and microfibrinous surfaces lead to cohesive failure deep (in SEM terms) within the polymer with extensive plastic deformation shown.

The energy associated with this plastic deformation is reflected in the higher fracture energy (peel strength).

At one level the enhanced adhesion to the microporous or microfibrinous surface can be accounted for by referring to the mechanical theory of adhesion. Interlocking between the polymer and substrate via the pores or fibres occurs. It is valuable, however, to consider in more detail *why* this should lead to plastic deformation and cohesive failure.

Near the interface, a microfibrinous substrate in some respects resembles a discontinuous fibre composite, formed from relatively high modulus, high tensile strength fibres (e.g. CuO) and relatively low shear strength polymer (P.E.). When stressed, high shear stress builds up at the fibre ends. This is shown mathematically by analysis of the stress distribution [12] or visually by demonstrations with photoelastic resins, Figure 4 [6]. Under the high shear stress at the fibre tips, the polymer will be expected to yield with plastic deformation moving into the bulk polymer until failure occurs. As failure occurs the stress situation leading to plastic failure is propagated along the peel front as peeling occurs [11]. The influence of surface topography on the local stresses at the interface was emphasised by Sharpe [12].

According to this model the enhanced adhesion of the microfibrinous substrates is associated with physical *discontinuities in the interfacial region* (the fibres) and the consequent local stress concentrations. Other interfacial discontinuities can lead in a similar way to enhanced adhesion. The sharp angles at the mouths of micropores act like this [6]. Even small interfacial bubbles cause discontinuities which can enhance adhesion. Stress concentration around such bubbles is to be expected from stress analysis and is observed using photoelastic resin [14].

Elastic energy dissipation. The emphasis in the previous section was on plastic dissipation of energy as a result of discontinuities at an interface. There are circumstances where the energy is dissipated viscoelastically, or even elastically.

Gent and Lin have shown that large amounts of energy can also be involved in peeling an *elastic* material from a rough surface [15]. The energy is essentially used for the elastic deformation of embedded filaments: this energy is lost because when the filaments become free, they immediately relax.

Gent and Lin experimented with rubber bonded to aluminium plates with regular arrays of cylindrical holes. The peel energy was low for the plates in the absence of holes. An energy balance analysis gives the ratio of fracture energy for peeling from the material with cylindrical pores G_a' to that from a smooth substrate G_a as

$$G_a' / G_a = 1 + 4 \phi l / a \quad (2)$$

where l is the pore length, a its radius and ϕ the ratio of pore area to total area of the plate [15]. Their experimental results demonstrated the essential validity of this relationship. Where pull-out alone occurred the work of detachment for their system increased by up to 20 times. Thus irreversible deformation is not an essential feature of enhanced fracture energy resulting from discontinuities at the interface.

3. ADHESION IN NATURE: THE GECKO

In recent years increasing attention has been turned to adhesion in the natural world [16]. Here examples can be found of durable adhesion in difficult environmental conditions which human technology is unable to rival. Barnacles and mussels provide obvious examples. Strong, but instantly reversible, adhesion to a wide variety of surfaces is shown by a large number of insects, spiders, and even lizards.

One such lizard is the gecko. This amazing animal is capable of running up vertical and inverted surfaces, attaching and detaching its toes in milliseconds, Figure 5(i). It attracted comment from Aristotle [17] and its "adhesion" has been the topic of much speculation and experimental investigation.

In contrast to the complex adhesives associated with marine organisms, such as barnacles and mussels, the gecko secretes no adhesive as such. As it can walk on smooth inverted glass and molecularly smooth silica, neither friction nor mechanical interlocking are requisites. Studies *in vacuo* show that small suction pads are not involved, but there is evidence that the surface energy of the

substrate, rather than its structure, determines strength of adhesion - geckos cannot adhere to PTFE. This points to intermolecular forces - van der Waals forces – as playing an essential rôle [18].

Examination of the foot of the gecko shows that it consists of a range of fine structures which are revealed at higher and higher magnifications, Figure 5(ii). The toes are covered with nanoarrays of hair-like setae (bristles) formed from stiff β -keratin. These further divide into hundreds of spatulae with nanoscale diameters. Each spatula ends in a leaf-like plate or pad which makes contact with the surface. This ultra-fine structural division is considered to be essentially linked to the gecko's adhesive ability [19].

Indirect evidence that finely divided structures, like those found on the gecko foot, are related to an animal's ability to climb smooth vertical surfaces comes from an examination of the structure of feet of other climbing animals such as spiders and flies. These too have finely divided structures: the heavier the animal, the finer the structure (Figure 6) [20].

Some authors rationalise the gecko's adhesion by invoking the "Principle of contact splitting" according to which splitting up the contact into finer and finer subcontacts increases adhesion [20, 21]. Chan et al.[21] explain this in terms of a simple peel test. A simple energy balance analysis shows that for peeling a non-extensible strip (width b) from a rigid substrate, the relationship between the peeling force applied, F , and the angle of peel (θ) is [22, 23]

$$F/b = G/(1 - \cos\theta) \quad (3)$$

where G is the peel energy (fracture energy), assumed to be independent of peel angle.

The argument of Chan et al. can be understood with reference to figure 7 In figure 7(i), the adhesive layer (grey) is continuous so (for a peel angle of 90°), the peel force will be

$$F = b G \quad (4)$$

Fig 4(ii) represents the situation where the adhesive has been split into n close-packed segments ($n = 16$ in the figure). Chan et al. point out that, *if all regions of a representative patterned area peel simultaneously*, the increase in interfacial width scales as $n^{1/2}$. (Essentially the total width peeled is being increased by this factor.) Thus, the total peel force F_n also increases as $n^{1/2}$ for a discontinuous interface as compared with a continuous interface:

$$F_n = n^{1/2} b G = n^{1/2} F \quad (5)$$

so with fine discontinuities at the interface, the peel force can become very large.

Whatever may be thought of this argument, the principle that "subdivision" at the interface can enhance practical adhesion has been recognised in the adhesion literature for a long time: adhesion to porous alumina, discussed above, is one example. Enhanced adhesion is the result of the presence of discontinuities at the interface which can enhance the energy lost in breaking the adhesive bond.

Thus contact of the millions of fine spatulae in the gecko's foot enable it to adhere strongly to walls or a ceiling. However, in order to walk it has to be able easily to overcome this adhesion. It does this by radically altering the angle between the spatulae and the substrate to which they are attached.

Consider equation 3: this predicts that

$$\text{as } \theta \rightarrow 0, \quad F/b \rightarrow \infty$$

$$\text{as } \theta \rightarrow \pi, \quad F/b \rightarrow P.b/2$$

At low peel angles, very high detachment forces are necessary, but these decrease sharply as the peel angle is increased.

When the gecko foot is attached to a substrate it is held in such a way that the setae and spatulae are kept at very low angle (θ) to the surface. A high force of detachment would be needed. When the animal releases its foot, it rolls its toes upward from the surface, "peeling" it off at a high angle, with a low force [24, 25].

4. BIOMIMESIS

The production of microporous (e.g. anodic oxides) and microfibrinous surfaces by chemical or electrochemical pretreatments has often been described and used as a way of producing strong, durable bonds, for example in the aviation industry. Finely patterned surfaces can also be produced by photolithography [21]. Figure 8 shows schematically how microporous (stage 4), or microfibrinous (stage 6), surfaces can be formed. These are sometimes described as mimicking biological surfaces – biomimesis.

Crosby et al. [26] have used lithographic techniques to produce patterned surfaces on crosslinked PDMS, consisting of low aspect ratio "posts" ranging from 25 to 250 μm in radius. Using a spherical silica probe to assess adhesion, they demonstrated that increases of up to four times the adhesion to non-patterned interfaces could be obtained.

Several groups, inspired by the nanostructure of the gecko's foot have attempted to produce synthetically equivalent structures. For example, Lee, Majidi, Schubert and Fearing at Berkeley have used a casting process, involving a polycarbonate microfilter, to produce a material with 42 million polypropylene fibres cm^{-2} , each fibre of length 20 μm and diameter 0.6 μm [27, 28]. After sliding under normal pressure this material develops a shear resistance (cf. gecko's foot) not shown by a control, non fibrous polypropylene. Such results provide a stimulus for further development of this type of biomimetic surface.

5. CONCLUSION

It was emphasised in the Introduction that an adhesive joint does not necessarily fail "at its weakest link", and as Dillard has elegantly demonstrated, identical joints can give quite different fracture energies under different loading conditions. It is hoped that this review will serve as a reminder that differences in stress states (loading conditions) at the interface can be achieved by the introduction of discontinuities. Some such discontinuities have been discussed which, in technological or natural systems, lead to an increase in adhesion.

6. Acknowledgements

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Table 1
Peel strength of low density polyethylene applied as a model hot melt adhesive to aluminium [6] and copper [11].

Substrate	Peel energy kJ/m ²	95% confidence limits kJ/m ²
Aluminium (degreased)	Very low	
Aluminium (Anodised H ₂ SO ₄)	1.97	0.19
Copper (polished)	0.21	0.06
Copper (microfibrous oxide)	1.62	0.14

Figure 1.

Altering the loading mode can result in (clockwise from top left) cohesive, interfacial, alternating, and oscillating failures. (reproduced from [2] by kind permission of the publisher, John Wiley & Sons)

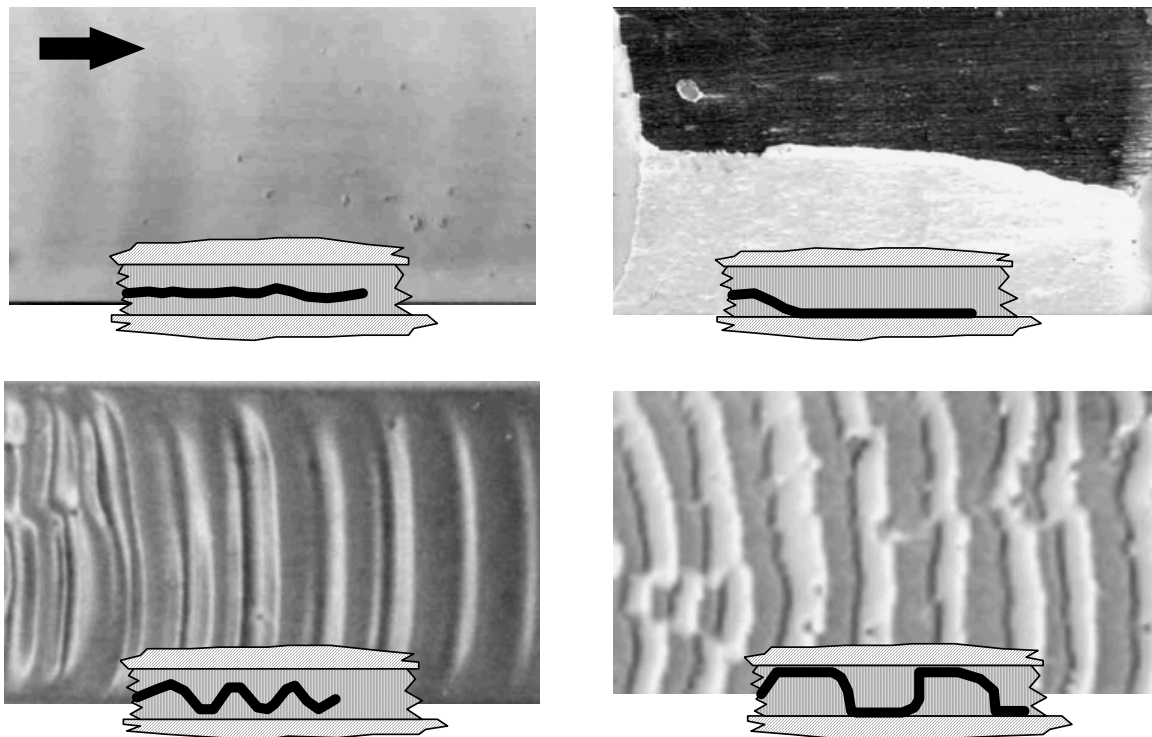


Figure 2
Structure of porous anodic oxide on aluminium (schematic).

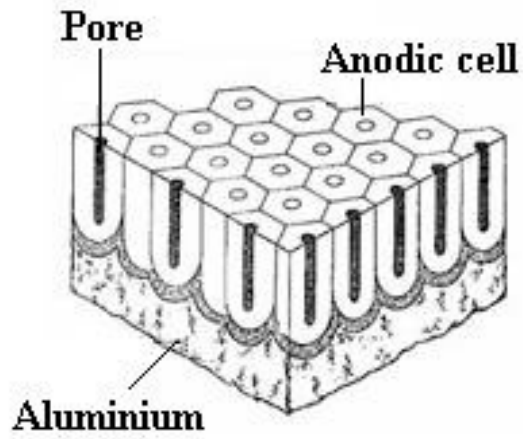


Figure 3
Microfibrous copper (II) oxide formed on copper [6]



Figure 4
Photoelastic model showing stress concentrations at "fibre" tips.[6]

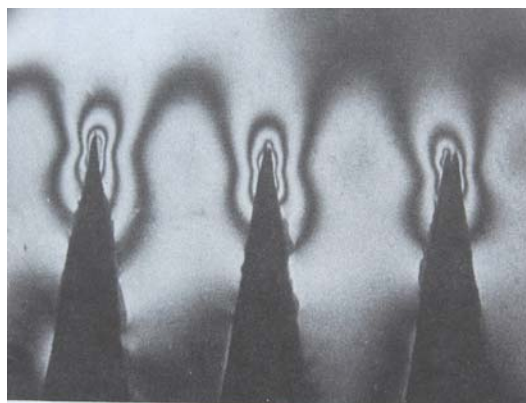


Figure 5

Gecko: (i) general view; (ii) structure of feet at progressively higher magnification (reproduced by kind permission of Dr Anne Peattie, Department of Zoology, University of Cambridge.)

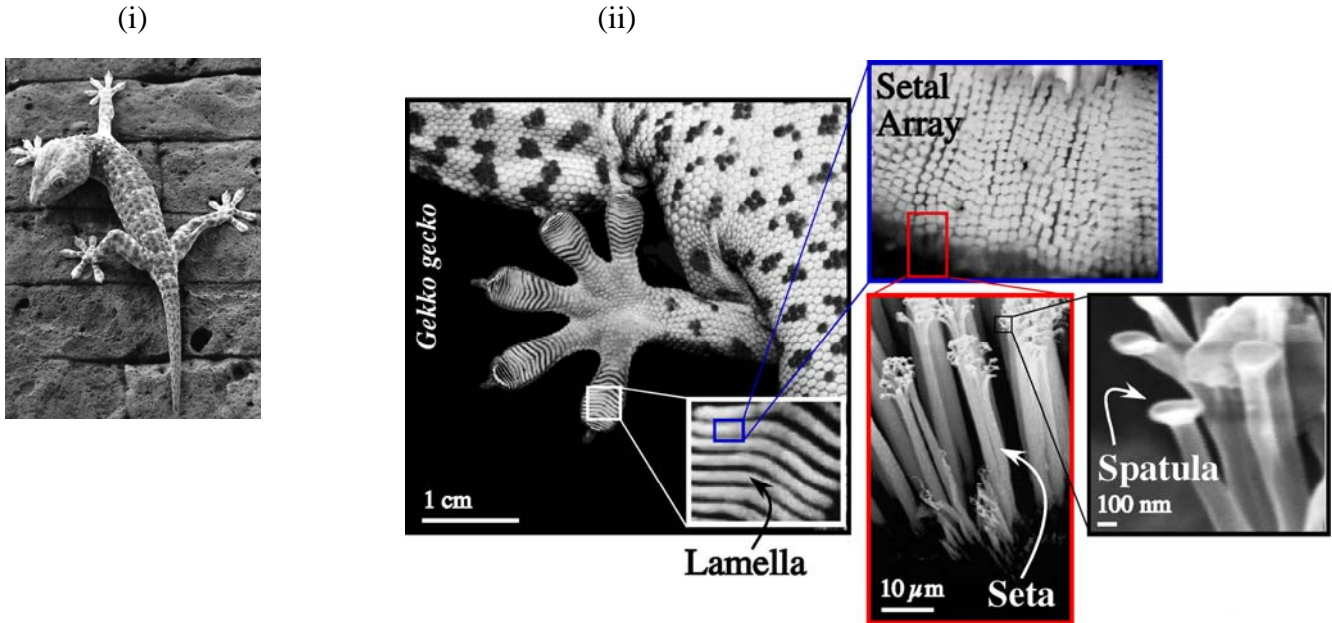
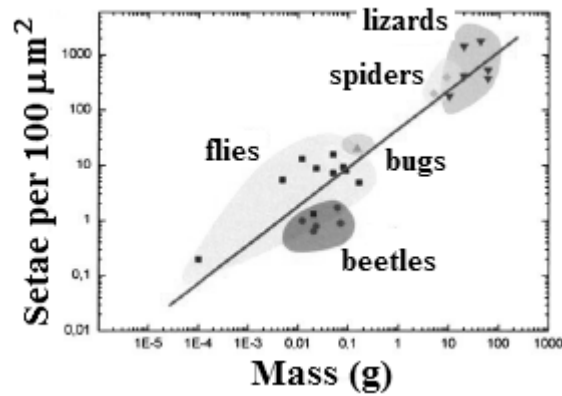


Figure 6.

Dependence of the terminal element density of the attachment pads on the body mass in hairy-pad systems of diverse animal groups [20]



**Figure 7 "Principle of contact splitting" after Chan [21].
Subdivision of adhesive layer in peel test.**

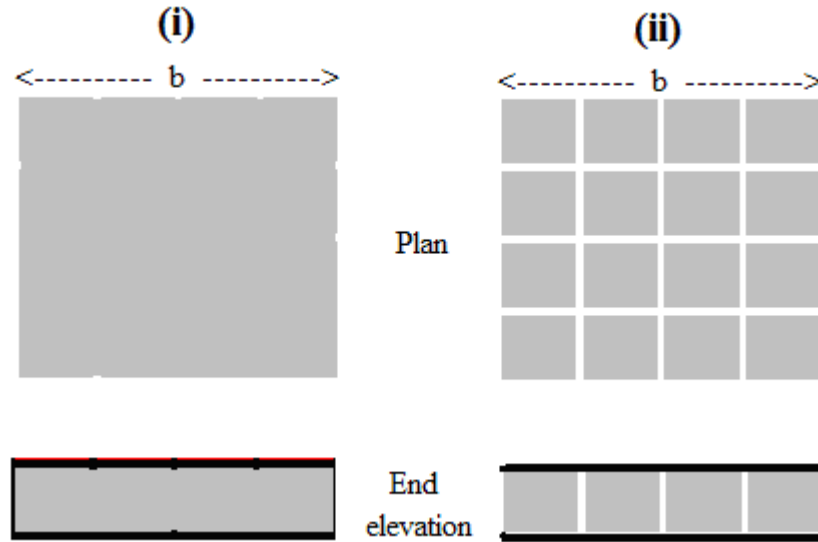


Figure 8 Photolithographic patterning (after Chan et al. [21])

