Surface Stress of Solids

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Introduction to Surface Stress

A distinction has to be drawn between stress at the surface and in the bulk of a material. That is, the stresses are not equal in the two zones. For structural applications, surface stresses, in general, are not the part of critical design parameters. For applications, like thin film or semiconductor devices, the surface is not too far removed from the bulk to induce effect on material properties.

Why is Surface Stress Important?

With the advent of semiconductors and nano-technology especially, surface effects and properties cannot be neglected. Semiconductors use oxide films; for example, silicon oxide is an important component in semiconductor technology. The techniques to form these oxide films include oxide deposition, plasma oxidation, and thermal oxidation [1]. As with many processing techniques, there are unintended consequences that may be either benign or malignant. As for semiconductor oxide films, the thermal stresses made by the high-temperature processing can lead to a degradation of reliability of the metal-oxide-semiconductor (MOS) devices [1]. In addition, processing of the raw material can create lattice mismatch. The lattice mismatch can create compressive stress at or near the surface. Experiments had been done showing intrinsic stress in silicon oxide films of 10 to 1000 nm thickness due to the lattice mismatch [1]. Considering that oxide films are use as gate insulators, the role or presence of surface stress cannot be ignored. In case of thin films, stress not only dictates the stability of the thin film system, but also controls

the electronic and magnetic properties of the thin film materials [2]. Surface stress or interfacial stress also plays a role in patterning of surface structures during epitaxial growth. Additionally, accumulated stress has been observed to impede the growth of epitaxial layer during deposition. Figure 1 illustrates this phenomenon. With this in mind, surface or interfacial stress should be understood in order to minimize defects or overall product quality.

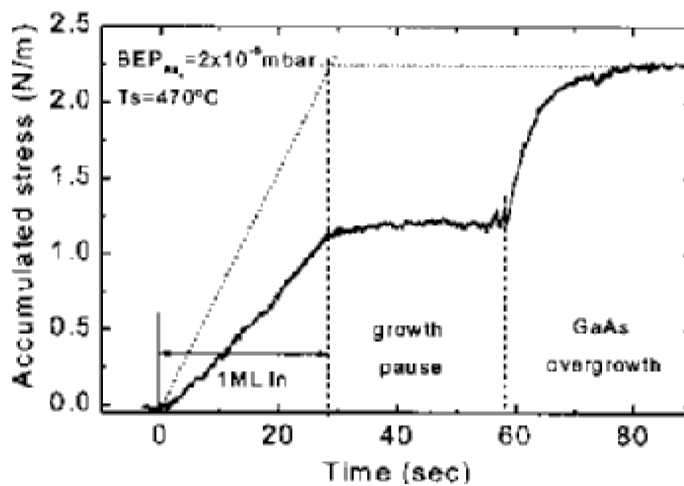


Fig. 1: Accumulated stress evolution during 1 InAs ML deposition, growth interruption and subsequent GaAs overgrowth, for [110] direction [3].

Definition of Surface Stress

To understand surface stress, its definition needs clarification. First, surface stress should be distinguished from surface free energy. Surface free energy is defined as the reversible work per unit area to create a surface, while surface stress is the reversible work per area to stretch a surface elastically [4]. Ibach [4] in his review of surface stress stated that the numerical difference between surface stress and the surface free energy can be as large as a factor of 3 for solid surfaces. Where surface free energy needs to be

positive in quantity, surface stress can be either a positive or negative quantity. Depending on applications, surface stress can be defined in one or two ways. Surface stress can be seen as the change in the bulk stress tensor near the surface or an interface; or, it is the difference between the electronic charge distribution near the surface and the bulk [4].

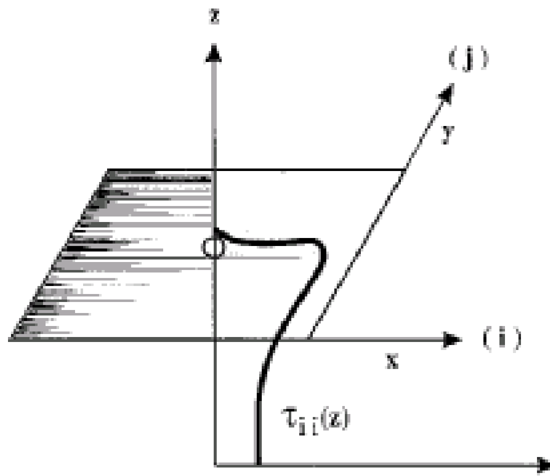


Fig. 2: Illustration of the variation of bulk stress $\tau_{ij}(z)$ near the surface (solid fat line) which defines the surface stress according to equation (1). The indices *i* and *j* denote the components of the stress tensor in the *x* and *y* direction, respectively [4].

A graphical representation defining surface stress as the change in the bulk stress tensor near a surface or an interface is illustrated in Figure 2. And surface stress is defined as the integral:

$$\tau_{ij}^{(s)} = \int_{-\infty}^{+\infty} \left(\tau_{ij}(z) - \tau_{ij}^{(b)} \right) dz \qquad (1)$$

In effect, the integral states that the surface stress, $\tau^{(s)}$, is composed of bulk stress tensor as a function of *z*, $\tau(z)$, which can be different from the bulk stress, $\tau^{(b)}$, in the vicinity of

the surface [4]. According to this equation, the unit for surface stress is force per unit length, as oppose to force per unit area for bulk stress. This definition along with the elasticity theory allows for the experimental determination of the change in surface stress, for example, through the bending of a cantilever beam. Ibach [4] went on to say that surface stress measurement is only meaningful if the test domain involves more than 10 to 50 atoms. This measurement method is what Ibach referred to as quasi-local surface stress. Qausi-local surface stress is more meaningful when inference is made about the macroscopic properties from microscopic structure.

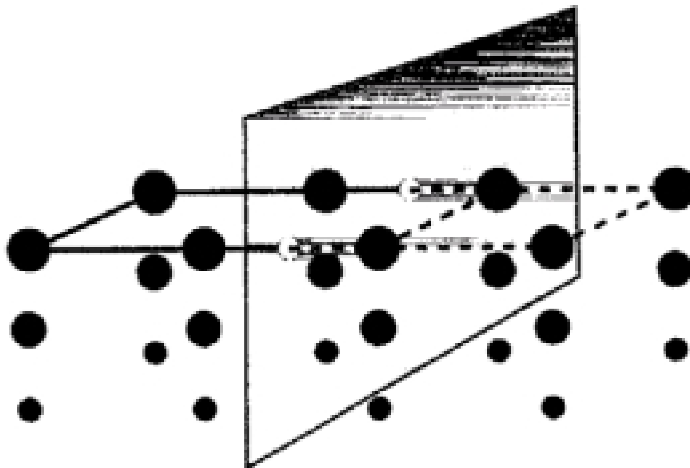


Fig. 3: Illustration for the discussion of the surface stress in terms of the electronic charge density between the atoms near the surface [4].

To understand surface stress from the view of electronic charge distribution and density, lets refer to Figure 3. Figure 3 illustrates that if all atoms and electronic charge density are removed from one side of the intersecting plane without allowing the electronic charge density to relax in response to the missing atoms, then surface stress is the sum of

the forces per unit length of intersection which are needed to keep the remaining atoms in place, minus these forces in the bulk [4]. With this definition, the types of surface stress, tensile versus compressive, can be further clarified. Typically for transition and noble metals, there are missing bonds on the surface. Hence, bond charges tend to move from above the surface into the selvage of the solid. That is, the charge is relocated to the area between first and second layer atoms. The backbonds of the surface atoms are then strengthen, and thereby becoming shorter [4]. This contraction between the first and second layer would lead to a tensile surface stress. Likewise, when deposition of materials is performed on a surface, this lead to an outward movement of electronic charge between surface atoms. As a result, compressive surface stress is accumulated. It is known that surface stress affects surface reconstruction, for example, from sp^3 electronic configuration to sp^2 configuration. Surface reconstruction will take place once an energy barrier is overcome. This barrier is the difference between the surface stress and the surface free energy. If absolute difference between the two is large enough, surface reconstruction occurs [4].

In addition to separating surface stress from surface free energy for solids, surface stress for liquid surface needs a brief clarification. Where surface stress and free energy are not equal for solids, they are equal for liquid surface. The reason is that the free energy does not change when the liquid surface is strained; that is, liquid shows no resistance to plastic deformation [4]. If the surface is expanded, atoms or molecules merely flow from the interior to the surface. The configuration of the surface atoms recovers to their previous state. This phenomenon is what is known as surface tension.

Measurement of Surface Stress

It is known that measurement of stress cannot be done directly, at least not effectively or practically. Subsequently, other parameters are measured to give the state of stress of a material. The parameter that is widely accepted is the measurement of strain to determine the stress level. However, the measurement of surface stress or residual stress has motivated experimenters to devise new method such as the use of acoustic waves. In this section, three methods of measurement of surface stress will be introduced, including a brief summary of the use of acoustic waves to determine surface stress.

Cantilever Bending

The cantilever bending method for determining surface stress is based on the understanding that a thin film substrate will bend as a result of deposition of a material. The means to measure the degree of bending may vary, but the principles of measurement are essentially the same. With deposition of a single monolayer, for example, the stress on surface will be changed and lead to the bending of the cantilever. The main thing to understand is that absolute stress measurement is not being made. It is rather the changes in surface stress that are determined [4]. Therefore, surface stress measurements require the characterization of both the unstressed surface and stressed surface. Two experimental means have been devised to detect the bending of the

cantilever. One involves the change in capacitance; the other uses laser to measure the degree of bending.

The Three Terminal Capacitance Method

The principle of this cantilever bending method is illustrated in Figure 4. A tube of diameter *d* delivers the material to be deposited onto the substrate surface. The substrate is mounted on one end while the other end is loose. The loose end becomes one of the two electrodes for a capacitor. As a result of the material deposition, the cantilever bends. As a result of the change in gap width between the two electrodes, the bending changes the capacitance. The bending also changes the radius of curvature of the cantilever. With these results, surface stress can be determined.

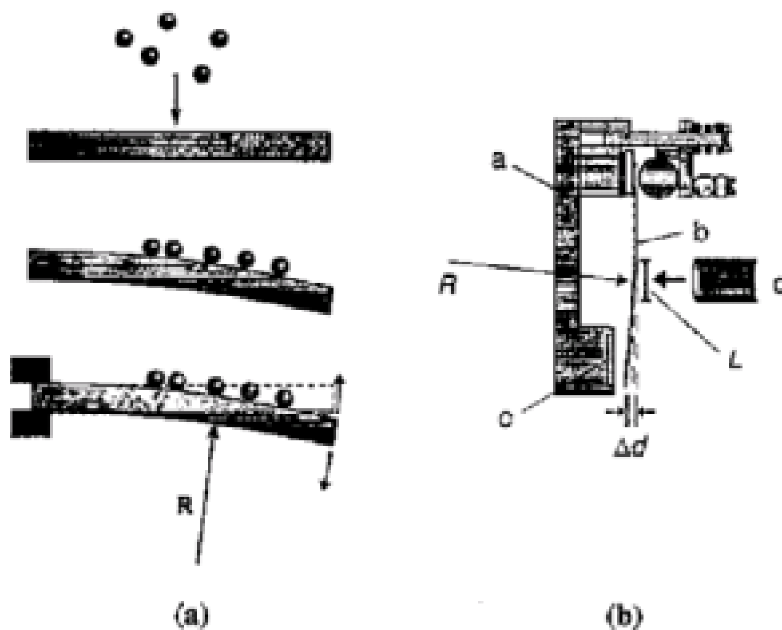
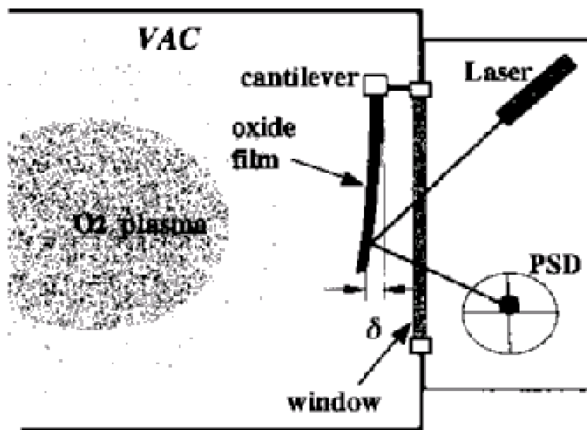


Fig. 4: Illustration of the principle of the cantilever bending method. Upon deposition of material on one surface, the stress is changed and the cantilever bends [4].

The three terminal capacitance method allows for extremely small changes of the capacitor gap to be measured. This small change can be less than 0.1 angstrom; the benefit of this is the freedom to use thicker samples of about 0.3 to 0.5 millimeter thickness [4]. In addition, it is found that the sensitivity of this method is limited more by vibrational noise and thermal drift then by the sensitivity of the detection. As Figure 4 suggests, the ability for the cantilever to bend depends on the spread of deposited material. Thus, cleanliness of the substrate surface is important to the accuracy of the experiment. For example, if only the surface directly facing the tube in Figure 4 is cleaned, then adsorption may only occur in that area. By this, bending will only occur in that area. Although Ibach [4] didn't mention the specifics of the experimental setup, it is safe to assume a vacuum setting was used so the cleanliness of the specimen surface was



not compromised.

Fig. 5: Schematic diagram of a stress measurement system. The laser and the PSD are directly fixed to the same flange to which the cantilever is mounted. The cantilever position is about 100 cm away from the center of the plasma. The stress is calculated from the deflection δ of the cantilever system [1].

Laser with Position Sensitive Detector Method

The laser method is similar to the above method in terms of experimental principles with the exception of how the cantilever bending is measured. Surface stress determination with laser is illustrated in Figure 5. This particular schematic employs the use of a position sensitive detector to measure the deflection of the substrate backside while the substrate is enclosed in a vacuum chamber where oxygen plasma is used to deposit an oxide film onto the surface. The surface stress, accumulated as a result of the oxide film, can be calculated with respect to the cantilever deflection as follow (Stony's formula):

$$\sigma = \delta E h^2 / 3L^2 (I-v) t \qquad (2)$$

where L and h are the length and thickness of a cantilever, E is the Young's Modulus, v is the Poisson ratio, t is the thickness of oxide layer. Typical of this experimental setup, the resolution of the cantilever deflection is less than 0.1 nanometer, and the cantilever thickness is about 4 microns [1]. Compared to the three terminal capacitance method where the specimen thickness can be 0.3 to 0.5 mm, the specimen preparation with this method is more crucial.

Acoustoelasticity

The use of ultrasonic waves, specifically the Rayleigh waves, to determine surface stress had been undertaken by Wei et al [5] recently. Wei et al used an isotropic elastic material, polymethylmethacrylate, for testing. The basic principle for this testing was based on the understanding that there was a linear dependence of the velocity change of

Rayleigh ultrasonic wave on the applied stress or deformation [5]. More specifically, the stress field influences the velocity of the ultrasonic waves. To verify the accuracy of the test, strain gages were simultaneously used to provide a secondary source of strain measurement with respect to the use of ultrasonic waves.

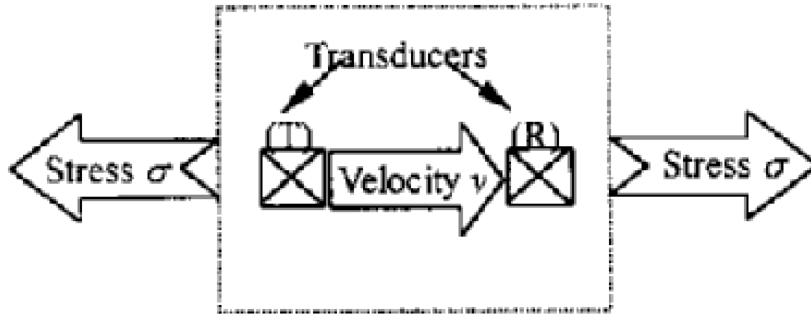


Fig. 6: Schematic diagram for acoustoelastic determination of surface stress on a uniaxial stressed solid [5].

Figure 6 provided a schematic of the test set up. A uniaxial stress was applied on a solid. The Rayleigh wave propagated from the transmitter to the receiver of the transducer setup. The applied stress and wave velocity changes were governed by the following equation:

$$\frac{\upsilon-\upsilon_o}{\upsilon}=K\sigma \qquad (3)$$

where v_0 is the velocity of the Rayleigh wave in the natural state of the material, and K is the acoustoelastic coefficient governed by the material constants such as density, elastic modules [5].

The experimental results found by Wei et al confirmed the equation to a good degree. This confirmation was illustrated in Figure 7 and Figure 8. The discrepancy between actual and theoretical results was attributed to the neglect for the stress perpendicular to the loading direction and the inability to take measurement close to the brim of the through hole in the test specimen [5]. This inability arose from the lack of small transducers and strain gage.

X-ray Diffraction

The use of x-ray diffraction to measure stress stands out among the aforementioned methods. The distinction arises from the fact that stress is determined by examining how the lattice planes are affected by the applied or residual stresses. By the same token as aforementioned methods, stress cannot be measured directly with x-ray diffraction. Only strain is measured to give inference to what the state of stress the material is experiencing. When an applied force is loaded onto a specimen, the lattice plane spacings of a polycrystalline material are affected. It is through this change in lattice plane spacings that strain is determined. More specifically, the change in lattice plane spacings causes a shift in the diffraction lines [6]. The diffractometer method allows the change in plane spacings be detected through the angular position of the diffracted beam. Cullity in his book has shown that stress, strain, plane spacings, and the angular position, 2θ, are related through the progression of the following equations [6]:

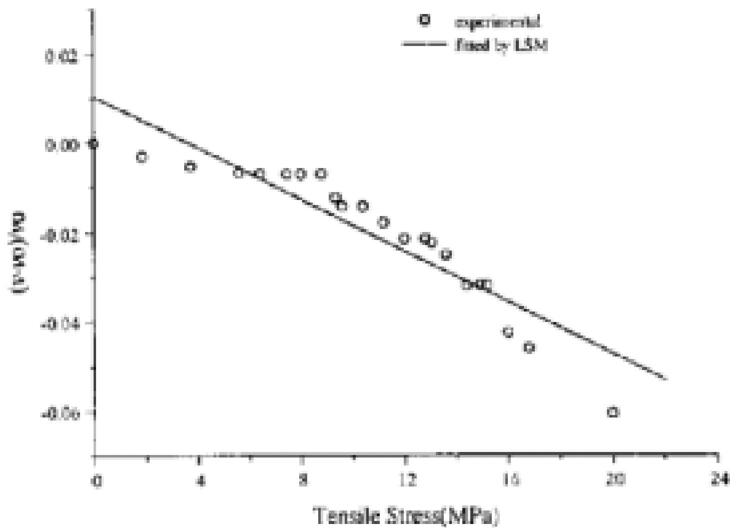


Fig. 7: Stress dependence of velocity of Rayleigh wave parallel to the stress direction [5]

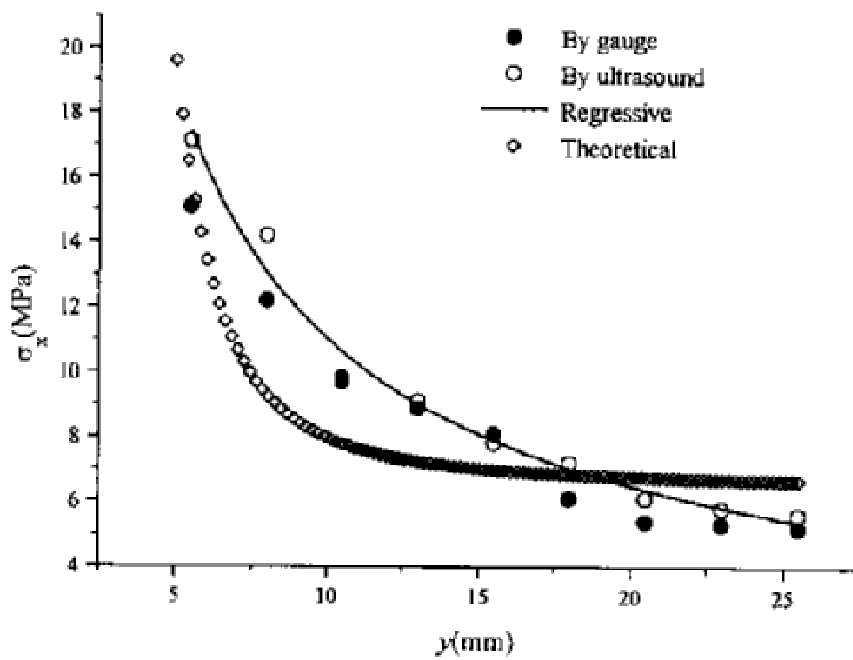


Fig. 8: Stress distribution in the direction of load [5].

$$\sigma_y = E\varepsilon_y \tag{4}$$

$$\sigma_\phi = \frac{E}{(1+\upsilon)\sin^2\psi}\left(\frac{d_i - d_n}{d_n}\right) \tag{5}$$

$$\sigma_\phi = \frac{E\cot\theta(2\theta_n - 2\theta_i)}{2(1+\upsilon)\sin^2\psi} \tag{6}$$

Figure 9 illustrates the basic principles of the diffractometer method for stress determination. The method comprises of the specimen, capable of being rotated about the diffractometer axis, an x-ray source, and a counter for receiving the reflecting beams. The standard diffractometer method usually requires two measurements to be taken [6]. The two measurements comprise of two different angles of Ψ. The angle Ψ is formed by line bisecting the angle made by the incident and reflected x-ray beams with respect to the normal to specimen surface. This is illustrated in Figure 10.

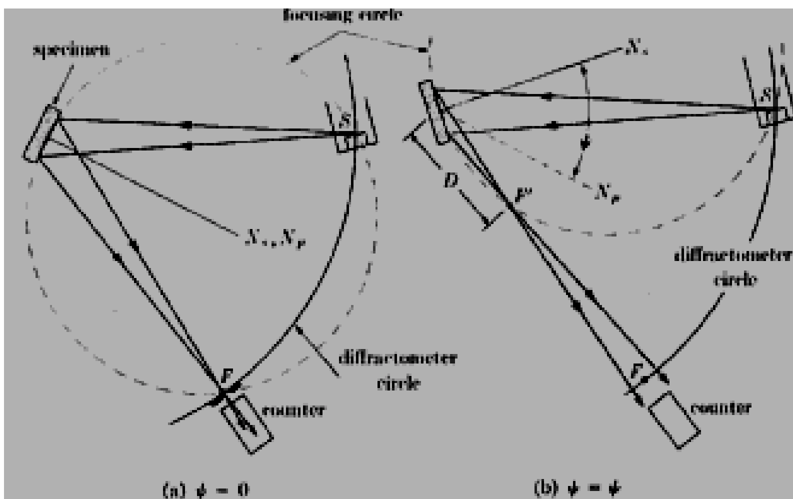
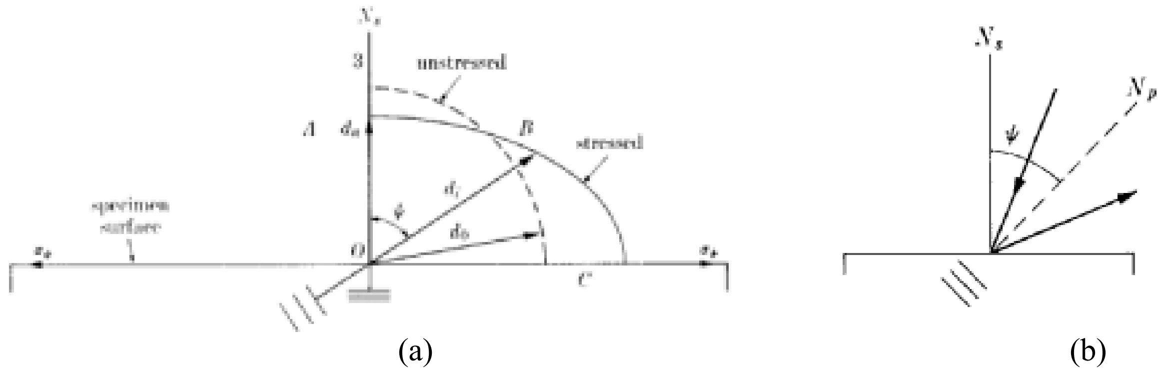


Fig. 9: Use of a diffractometer for stress measurement [6].



(a) (b)

Fig. 10: Vector diagram of plane spacings *d* for a tensile stress σ_ϕ [6].

Another distinction that x-ray diffraction has is its ability to measure surface stress while a mechanical component is in service. In other word, x-ray diffraction can be a nondestructive way to determine stress so long as the specimen fits into the test chamber or the test setup environment. Additionally, x-ray diffraction allows for repeated measurements on the same specimen without compromising the specimen [6]. This is useful if a critical part in an engineering system is known to accumulate residual stress. Hence, the critical part can be replaced in advance of any catastrophic failure.

As with any testing method that rely on the specimen surface for measurements, the surface thus needs to be clean and smooth. If the surface is rough, the incident beam may be reflected in a different direction away from the diffractometer counter. In addition, the high points on a rough surface have stress that is different from the bulk of the material [6]. Hence, to reduce error in measurement, a rough surface should be avoided for x-ray diffraction measurements. Grinding and machining are not advised as surface preparation methods. These two methods are known to introduce large stresses to depths

of at least 125 microns [6]. Electrolytic polishing is a recommended surface preparation method.

Practical difficulties do exist when using x-ray diffraction for stress determination. Certain conditions include large grain size, preferred orientation of specimen, and plastic deformation can affect the accuracy or impede the use of x-ray. Large grain size for example can make the diffraction line spotty or distort the line position. If the grains are excessively large, then the use of x-ray may be impossible. Some industrial products where metals may have large grains include metal parts that underwent annealing or sintering as in case of metal powder injection molding. One of the problem associated with preferred orientation is that diffraction line may be strong at $\Psi = 0°$ and absent at $\Psi = 45°$, or vice versa [6]. When a specimen is plastically deformed in a particular way by some processes, the x-ray method does not reveal the true macrostress. Cullity in his book explains that it is the pseudo-marcostress that is determined through x-rays. As an example, a specimen that underwent quenching, the residual stress in the outer surfaces is due to plastic flow in the interior [6]. Therefore, the location or section where x-rays are exposed should be selected with care when possible. However, the accuracy of x-ray diffraction is not affected in regions away from the plastically deformed area.

Factors Affecting Surface Stress

Presence of Vacancies

Vacancies and vacancy clusters at or near the surface have an effect on the residual stress experienced by the material. To simplify the matter, a few assumptions have been made: (a) the material is monatomic so there are no alloying effects such as surface segregation, (b) all changes in the surface structure at the surface are elastic, and (c) atmospheric pressure and low temperature are assumed so that the free energy is simply the internal energy [7]. Surface stresses are the result of atomic interactions in the bulk, though opposite in the type of constraint. For instance, if the bulk atoms are in compression, the surface atoms are in a counterbalancing tensile stress. This is so that the free energy of the system is zero.

Vacancies or vacancy clusters that originate at the surface create a compressive stress at the surface, which reduces the initial surface stress. Where as, if the vacancies are below the surface, a tensile stress is experienced at the surface, increasing the total stress at the surface. This is illustrated in Table 1 and Figure 11. Therefore, in order to minimize the surface stress of a system, vacancies should be introduced to the surface layer of atoms.

Relaxation of the Material

According to Marcus *et al*, surface stress (S_s) at the surface of a macroscopic crystal is usually introduced as the rate of change of energy of the crystal due to in-plane strain per

Table 1: The surface stress or change in surface stress and formation energy for a variety of configurations [7].

Configuration (periodicity 40, rows 20; surface energy $\gamma = 1.41$ J/m^2)	Surface stress f or Δf (N/m)	Vacancy or cluster formation energy (eV)
No defects	6.78	1.16 (bulk vacancy)
A, vacancy, 1st	−0.77	0.45
B, vacancy, 2nd	0.74	1.30
C, vacancy, 4th	0.40	1.16
D, vacancy, 8th	0.36	1.16
E, 2 vacancies, both 1st	−0.73	0.45
F, 2 vacancies, 1st, 2nd	−1.52	1.35
G, 3 vacancies, 1st, 2nd, 3rd	−2.88	2.02
H, 7 vacancy cluster, 8th	1.03	3.66

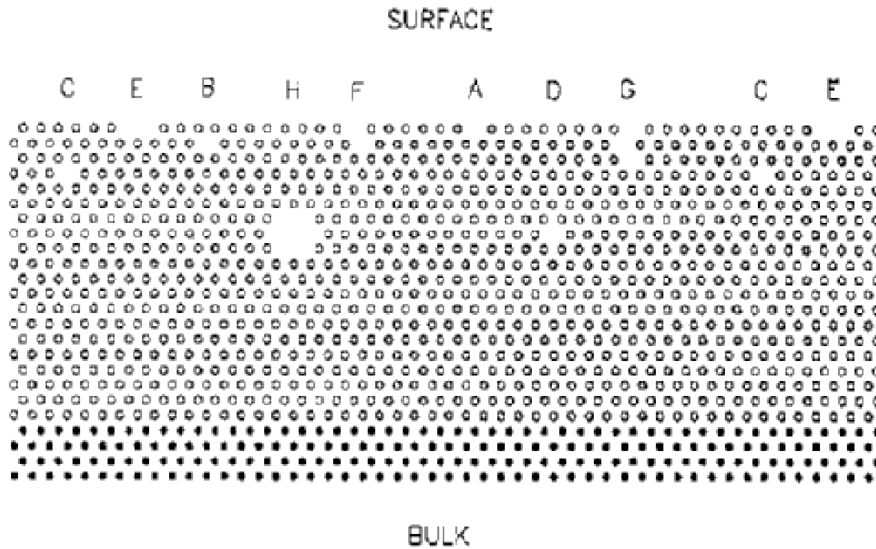


Fig. 11: The set of atoms for a typical calculation showing the configurations listed in Table 1. The solid atoms are held at the bulk equilibrium spacing and the open 20 rows of atoms are permitted to relax. The defects are taken as a periodic array, in this case with periodicity of 40 atoms, and the stress is calculated midway between the defects [7].

unit of surface area [8]. A relationship exists between the surface stress and the lattice constant (a) of a crystal structure. This inverse relationship is as follows:

$$S_s \propto \frac{1}{4A} \quad (7)$$

where $A=a^2$. So if the lattice constant of a particular crystal structure can increase, than the surface stress experienced by that particular crystal will decrease. This is exactly what happens during relaxation of a material.

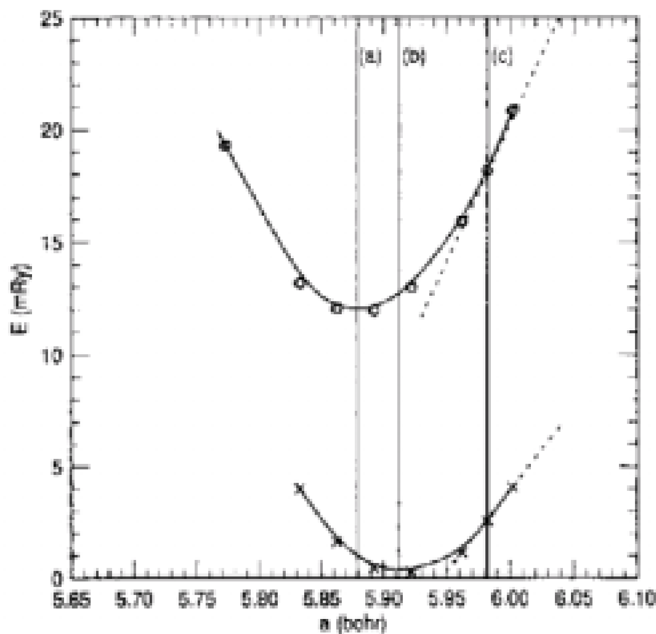


Fig. 12: Comparison of the total energy of a fully relaxed material with a partially relaxed material [8]

During the relaxation process, dislocations are annihilated which in turn reduces the energy of the system. Dislocations create a compressive stress in the bulk, which translates to a tensile stress at the surface: to keep the free energy of the system at zero. By removing dislocations within the bulk, the surface stress is minimized. Full relaxation of the material causes the surface stress of the material to be at a minimum. Figure 12

compares the total energy of a fully relaxed material with a partially relaxed material. From this figure it can be seen that a larger lattice constant translates to a lower total energy.

Conclusion

In this introductory review of surface stress, the following observations are made:

1. Surface stress is present and should be considered especially in thin-film system or semiconductor devices.
2. Surface stress is measurable with several methods.
3. Internal defects such as vacancies or vacancy clusters can lead to surface stress, while relaxation of the material serves to minimize surface stress.

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