Topical Review

Intermolecular and surface forces in atomic-scale manufacturing

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Abstract

Atomic and close-to-atomic scale manufacturing (ACSM) aims to provide techniques for manufacturing in various fields, such as circuit manufacturing, high energy physics equipment, and medical devices and materials. The realization of atomic scale material manipulation depending on the theoretical system of classical mechanics faces great challenges. Understanding and using intermolecular and surface forces are the basis for better designing of ACSM. Transformation of atoms based on scanning tunneling microscopy or atomic force microscopy (AFM) is an essential process to regulate intermolecular interactions. Self-assemble process is a thermodynamic process involving complex intermolecular forces. The competition of these interaction determines structure assembly and packing geometry. For typical nanomachining processes including AFM nanomachining and chemical mechanical polishing, the coupling of chemistry and stress (tribochemistry) assists in the removal of surface atoms. Furthermore, based on the principle of triboelectrochemistry, we expect a further reduction of the potential barrier, and a potential application in high-efficiency atoms removal and fabricating functional coating. Future fundamental research is proposed for achieving high-efficiency and high-accuracy manufacturing with the aiding of external field. This review highlights the significant contribution of intermolecular and surface forces to ACSM, and may accelerate its progress in the in-depth investigation of fundamentals.

Keywords: intermolecular and surface forces, atomic-scale manufacturing, transformation of atoms, AFM nanomachining, chemical mechanical polishing, triboelectrochemistry

1. Background

Manufacturing is the core technology that promotes human development, which can provide people with products that meet their material and spiritual needs. The development process of manufacturing technology can be divided into three stages in essence [1], as shown in figure 1. The first stage (Manufacturing I) is a manual forming process based on technical experience, and its machining accuracy is in the millimeter scale. The second stage (Manufacturing II) is controllable manufacturing based on machine precision, most of which is in the submicron scale. The third stage (Manufacturing III) is the direct manipulation of atoms to achieve atomic removal, transfer or addition in the atomic and close-to-atomic scale, also known as ACSM.
With the gradual improvement of human demand, the requirements for manufacturing accuracy in some fields, such as chip manufacturing [2], quantum bits [3], spin-based logic devices [4], and other emerging fields [5, 6], have reached the atomic scale, which bring great difficult challenges. The various manufacturing methods currently used by the industry are still included in Manufacturing II. The essence of most currently precision manufacturing methods is an extension of traditional manufacturing. The theoretical basis of their manufacturing system is still based on classical physics and chemistry, including classical elastic-plastic mechanics, fracture mechanics, thermodynamics and so on. There is an essential difference between Manufacturing III and the first two stages, and its theoretical basis and process characteristics are different from the manufacturing methods commonly used in the industrial production. The manufacturing precision and scale are approaching the atomic level from the nanometer level, which is only the apparent difference between the second stage and the third stage. The more essential difference is that the basic theory of Manufacturing III is based on the quantum mechanical system. Quantum mechanics, intermolecular forces, and surface-interface forces have a decisive impact on fabrication precision and scale in Manufacturing III which were ignored in Manufacturing II.

With the efforts of numerous researchers, ACSM has made great progress [7], but ACSM still faces great challenges. On the one hand, the machining accuracy is no longer controlled only by machine accuracy, but needs to consider quantum mechanics and intermolecular force. This leads to the uncertainty and instability of ACSM machining accuracy. On the other hand, although some ACSM methods, such as scanning tunneling microscopy (STM) and atomic layer deposition (ALD), can achieve the manipulation of single atom or atomic cluster, they cannot achieve stable and low-cost batch industrial application. This makes Manufacturing III represented by ACSM not as convenient and efficient as Manufacturing II. The accurate description of the influence law of quantum mechanics, intermolecular and surface force on ACSM is very important to further improve the manufacturing accuracy and processing efficiency of ACSM, and may provide significant reference for the proposal of new ACSM methods in the future.

When the machining accuracy or machining size reaches the atomic or near atomic scale, the atomic effect become critical. Therefore, quantum effect should be considered in atom transfer, energy beam-matter interactions and multi physical field applied atomic machining.

Quantum mechanics uses Schrodinger equation to describe the state of atom–atom, atom–nucleus, atom–electron,
atom–field systems. For different systems, different Hamiltonians should be proposed. Studying atom–atom system could better explain the interatomic bonding including covalent bond and ionic bond. Particle beam processing could be explored by studying atom–nucleus system. The atom–nucleus interaction could describe the atoms removal after being bombarded by particles. Proton LIGA (the abbreviation of lithography, galvanoformung, and abformung in German, which means the combination of deep lithography, electroforming and injection molding) technology is relevant with ACSM processes. Atom–electron systems could represent the atom–electron beam interaction. Because of electron scattering, energy could be transferred from electron to the atoms, which may cause interatomic bond breaking and eventually lead to atom removal. Electron beam lithography, electron beam-induced modification or deposition and ion beam lithography is related with ACSM processes. Due to the electromagnetic feature of light, the photo-matter interactions could be considered as the interaction between atoms and electromagnetic field. With the application of multiple physical fields at the atomic scale, the manufacturing capacity could be improved in thermal ALD [9], thermal assisted SPM tip-based nanofabrication [10], and magnetic field assisted machining [11]. It will be of great significance to study the ACSM manufacturing under multi-physical fields.

Intermolecular forces are part of electromagnetic forces. The intermolecular forces manifest as surface forces between large particles or extended surfaces. A macroscopic performance of these surface forces between matter in a vertical direction is the adhesive force, and lateral direction is the friction force. It comprises van der Waals and hydrogen forces.

The van der Waals force is an interaction among neutral molecules. It comprises three different forces: orientation, induction, and dispersion forces [12]. Orientation force describes the interaction between the dipole of one molecule and that of another. It only exists in the interaction of dipole molecules. Induction force describes the statistical time average interaction between the instantaneous dipole of one molecule and the permanent dipole of another. It applies to the interaction between dipole molecules and any other molecule. Dispersion force describes the statistical time average interaction between the instantaneous dipole of two molecules. It applies to the interaction between any molecule. The van der Waals force has a great influence on the interaction of surfaces in the ACSM process. The effective utilization of van der Waals force can achieve some special functions, such as superlubricity. By considering van der Waals surface force and surface energy, Zheng et al [13] estimated the friction stress between graphite island layers, and confirmed that self-retraction phenomenon of graphite island is superlubricity [14]. However, macroscale superlubricity in air is still an extraordinary challenge. Recently, macroscale superlubricity on macroscale flat surfaces has been realized for the first time on graphene coated surfaces under van der Waals forces, which is elucidated by molecular dynamics (MD) simulations and verified by experimental measurement [15]. Structure superlubricity may have potential application in micro–nano electricity generator, mechanical hard disk, and aerospace bearing as shown in figure 2 [16, 17].

Hydrogen bond widely exists in the interaction between molecules and water. It allows ethyl alcohol to be mutually soluble with water in any ratio. The hydrogen atom loses part of its charge by bonding with the electronegative atom (O, F), and the negatively charged hydrogen atom attracts the second negative ion to form a hydrogen bond. Usually, the intermolecular hydrogen bond has a longer equilibrium distance than the covalent bond, and is shorter than the distance forming van der Waals bond. For example, the OH covalent bond is approximately 0.10 nm, OH hydrogen bond is approximately 0.17 nm, and the van der Waals bond is approximately 0.26 nm [12]. This indicates that the hydrogen bond energy is between covalent and van der Waals bonds. With the development of ultra-high vacuum and ultra-low temperature atomic force microscopy (AFM)/STM, Zhang et al find lines at the position of hydrogen bonding in 8-hydroxyquinoline (8-hq) molecular in the scanning image [18], which may be a real-space visualization of hydrogen bond [19, 20]. By considering hydrogen bonding effect, Luo et al discovered the superlubricity phenomenon promoted by hydrated multivalent ions [21]. It may have potential application in hydration lubrication systems.

Another significant surface force theory in ACSM is the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory [22]. This theory considers van der Waals interaction and electric double layer repulsion. The DLVO theory is a theory about colloid (SOL) stability, which is a classical explanation of the
charged colloidal solution theory. It quantitatively explains the aggregation of aqueous dispersion system, and describes the force of charged surface interacting through the liquid medium. With the development in self-assembly, the DLVO theory is widely used in explaining various molecular self-assembly process of ACSM. Numerical simulation provides a way to explore the influence of intermolecular forces on ACSM [23–25]. For the manufacturing methods in the Manufacturing II, such as turning and grinding, finite element method (FEM) is usually used for numerical simulation. The typical characteristic of FEM is the assumption that the material is a uniform continuous medium in a certain range, which is applicable in the machining with the machining accuracy above submicron. However, for ACSM, its manufacturing accuracy is at the atomic or close-to-atomic scale. It is usually inappropriate to generate grids based on the continuous medium assumption. Instead, MD is more suitable for the complex dynamic processes in ACSM than FEM. In MD, the position of atoms in the system is updated by the force with other atoms, which is dominated by the potential function. Therefore, the accurate potential function is more important for the accuracy of MD in ACSM. van der Waals forces is inversely proportional to the sixth power of distance. Considering the Pauli repulsion and van der Waals interactions, the potential energy can be provided in Lenard–Jones potential form as expressed in equation (1) [26]:

\[ U(r) = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right), \tag{1} \]

where \( \sigma \) represents the equilibrium separation, and \( U(r) = 0 \). Its equilibrium distance \( r_e = 2^{1/6} \sigma \) with minimum energy equals \(-\varepsilon\). MD can be used to simulate the atomic scale material removal process in ACSM, such as ultra-precision machining (UPM) [27] and chemical mechanical polishing (CMP) [28]. Limited by the computing power of the computer, the number of atoms that MD can calculate is usually no more than 1 million. However, in a recent study, through the introduction of machine learning, the number of atoms that MD can calculate has exceeded 100 million [29], which will greatly promote the further application of MD in ACSM in the future.

The first principle is a quantum mechanics simulation method that can be used in ACSM to study the interaction between atoms. In a broad sense, MD also belongs to the category of first principles, but usually first principles refer to the calculation method based on density functional theory (DFT). Its basic idea is to regard the atomic scale system as a system composed of multiple electrons and nuclei, and deal with the problem to the greatest extent ‘non empirically’ according to the quantum mechanics. DFT contains much fewer atoms than the tens of thousands calculated by MD, but it can accurately calculate the bond length and bond angle [30], which is suitable for the simulation of the deposition of atoms on the surface in ALD [31, 32]. DFT allows researchers to determine the adsorption mechanism and adsorption strength of the new atomic layer on the substrate surface, which can provide effective help for the determination of the optimal ALD process.

In this review, the important contribution of the intermolecular and surface forces in the ACSM process has been discussed, which can help understand the manufacturing process, and probably develop a new method or improve the performance. Section 2 reviews the major types and their mechanism of ACSM, and expounds the important role of intermolecular forces involved in different types of ACSM. Section 3 summarizes the basic principle of the ACSM process as a general thermal activation model, and proposes the potential method to further decrease the reaction barrier and achieve higher efficient and higher accuracy manufacturing with the aid of an external field.

2. ACSM and the involved intermolecular forces

Generally, ACSM involves the entire processes for converting raw materials into desired products by transforming, removing, or adding materials at the atomic and close-to-atomic scale, indicated by three basic approaches as atom transformation, additive manufacturing, and subtractive manufacturing. This section explains the basic mechanisms of the basic approaches and explains how the key interactions determine the atomic-scale manufacturing process.

2.1. Atoms transformation

Atom manipulation experiments generally relies on the STM and AFM. Atomic transformation is the basic manipulation method to immigrate the atom from one position to another, which is probably the most available approach to achieve direct single atom manipulation in the current study.

2.1.1. Atoms transformation with STM. The manipulation of atoms significantly relies on the molecular interaction between tip and target atoms. The first atomic manipulation experiment was achieved by moving Xe atoms on a Ni surface to form a logo of ‘IBM’ using STM [33], as shown in figure 3(a). STM is one of the scanning probe microscope techniques, which using the feedback of tunneling current for atomic scale imaging, as
well as atom manipulation. Typical manipulation experiments using STM include lateral and vertical manipulations.

For lateral manipulation, the atoms can be pulled or pushed by the tip by means of the Pauli exclusion or van der Waals interactions [34]. For vertical manipulation, an energy barrier, similar with the Lennard-Jones potential, requires to be overcome to transfer the atom from the sample surface to STM tip [35]. The interaction potential of the atom between sample surface and tip illustrates a finger-like shape with two potential wells. One is the initial adsorption site near the sample, and the other is near the tip’s apex surface. When the tip approaches the target atom, the atom can move to the deeper potential well, and the tip can absorb an atom because of stronger attraction [36], as shown in figure 3(b). This process is generally with the help of tip-sample bias [37]. The release process, where the atom on the tip migrates to the surface, can be achieved by applying a reverse voltage to overcome the energy barrier between the potential wells.

2.12. Atoms interchange with AFM. AFM is also a kind of scanning probe microscope technique, which used the interaction information between the tip and sample for surface topography imaging. It is also suitable for directly force measurement and atom manipulation. The main difference between AFM and STM for imaging is the feed-back signals. Thus, STM measured the tunnel current, which is sensitive to distance and image, while the AFM measured the tip-surface interaction force that includes the van der Waals, Pauli exclusion, electrostatic, electrical double-layer, hydration, and hydrophobic forces in water environment. It provides broader applications than STM because the sample is not limited to conduction. A diverse choice of probe and sample materials makes it possible for complex atomic operations.

Typical work to achieve atom transformation is similar with STM [38]. It concludes lateral and vertical manipulation manners. In addition, Sugimoto et al [39] discovered the interchange manipulation manner using AFM. The experiments were performed in the frequency modulation mode. Commercial silicon cantilever with sharp tips was utilized to image the Sn/Si(111)(√3 x √3)R30° surface. As discovered in the experiment, when the tip of the AFM (Si or covered with Sn) gradually approached the surface, a threshold energy inhibited the interchange of atoms between the tip and the sample surface. With the mechanical interaction increase, the threshold would drop below a certain value and allows the interchange of Sn and Si atoms with the thermal activation at room temperature. The interchange between Sn (Tin) atom and Si (Silicon) atom relied on the formation of a transition structure, which could provide a small potential barrier between the two minimum potential well positions, and allow a thermally activated atoms to interchange. The formation of the transition structure, and minimum potential well can be distinguished from the force-distance curve.

Here, the double potential well can be distinguished from the retraction curve (illustrated in figures 4(d) and (e)). The second potential well (at 0.3 nm) originates by the van der Waals force and determines the physical adsorption of atom. Further, the first potential well, which is very close to the surface, was formed after reaching the (Pauli) repulsion region. It originates from the formation and break in chemical bond of the transition structure. This is an indication for successful interchange of atoms.

2.2. Additive manufacturing

Additive manufacturing is a potential manufacturing process in the industry. At the macro scale, additive manufacturing mainly refers to 3D printing; however, at the atomic scale, additive manufacturing includes new manufacturing processes such as a self-assembly and ALD. Atomic-scale additive manufacturing can prepare some nanostructures or modify the surface of microstructure that cannot be achieved by subtractive manufacturing.

2.2.1. Self-assembly. One of the typical additive manufacturing in atom or close-to-atom scale is the Self-assembly. It describes a process where pre-existing components form self-organized structures by means of the interaction forces without human intervention. Self-assembly has been widely studied in macro and atomic scale manufacturing. Herein, we mainly introduce the atomic scale self-assembly.

Currently, some noncovalent or weak covalent interactions are used to guide atomic-scale particles self-assembly process, such as van der Waals [40–42] and depletion [43–45] interactions. Under the above interactions, atomic-scale particles move close to each other until they reach the steady state position with a complex balance between the attraction and repulsion to form an atomic-scale structure.

Take for example the self-assembly of amphiphilic molecules (surfactant molecule). The Self-assembly state can be described as a thermodynamic process, and the strength of interaction determines the aggregate concentration distribution and critical micelle concentration. The packing geometry of self-assembly is also influenced by the intermolecular interaction strength. The competition between the repulsion and attraction interactions determines the optimal headgroup area of the macromolecule. The Optimal headgroup area, volume of chain, critical chain length, determines the packing geometry. As the dimensionless packing parameter increases, the packing shape can evolve from sphere, cylinder, and bilayer [12].

Capillary force is a convenient van der Waals interaction used in self-assembly, especially in inducing nanorod assembly [46]. When the solution containing particles is dried, the adjacent particles are pulled together by a force as the solution molecules evaporate [47]. In the process of self-assembly, the particles move to the ordered region in the solution driven by capillary force [48]. The well-ordered monolayer or multilayer structure can be obtained by controlling the evaporation rate of the solvent.

The depletion attraction, as an entropic force, plays a critical role in the multimodal-size-particle distribution system to achieve the self-assembly [49]. When the nanoparticles are
close enough in solution, the volume regions between macromolecules are too small to be occupied by other particles. Then the adjacent macromolecules will approach each other because of the increase of osmotic pressure. Nanoparticles are close to each other because of the depletion attraction to increase entropy of the system, to complete the self-assembly process as illustrated in figure 5 [50]. The depletion attraction has been widely adopted in the study of self-assembly of colloidal particles [43, 51, 52]; however, when the size of the particles to be assembled is similar to that of the particles to provide depletion force, it becomes more difficult to use depletion attraction for self-assembly.

Host–guest assembly is a promising non-covalent interaction self-assembly method, which refers to a manufacturing process that forms inclusion complexes between the macrocyclic hosts and molecule guest in a highly-controlled and cooperative manner [53]. The special structures gives the macrocyclic hosts the ability to reversibly encapsulate molecule guest [54], which has a great application value, such as drug delivery [55]. In the field of tribology, based on the principle of host–guest assembly, Tan et al [56] achieved microscale superlubricity (the sliding friction coefficient was at 0.001 level, and the energy dissipation was negligible) by building the ordered structures of fullerene derivatives, as illustrated in figure 6. The ordered structures were achieved by assembling both macromolecule template and fullerene derivatives on graphene, by means of van der Waals forces and π-bonding assembly. This study extends the fullerene applications in the field of solid lubrication, and provide a new way to explore the friction mechanism at the molecular level.

2.2.2. Atomic layer deposition. Another typical additive manufacturing is the ALD, which is capable of generating thin films with single molecular layer deposited from the vapor phase [57]. ALD relies on sequential and self-limiting chemical reactions, mainly, ALD developed from chemical vapor deposition technology. The feature of ALD are the sequential and self-limiting chemical reactions between the alternating particles, separated by purging periods with inert gas, with the surface to form a desired atomic-scale and uniform thin film as illustrated in figure 7.
The most important advantage of ALD is the atomic-scale film thickness. The chemisorption layer thickness of each single deposition cycle is 0.01–0.3 nm, depending on the process [58]. Meanwhile, the other advantage is the extreme smooth and continuous film, because of the self-limit nature. The surface reaction sites limited the reaction process, which stops when there are no free surface reaction sites available. The above excellent characteristics apply to the preparation of 3D nanostructure with no effect by the high aspect ratios and shadowing [59].

Currently, the most common materials chosen to been grown by ALD are oxides, nitrides and sulfides. Some pure metal elements such as Li and Mg have been used as the ALD grown material. The limit of the availability of other materials is that there are no suitable reaction pathways because of the requirements on the self-limiting reaction. Some important materials in the industry, such as Si, SiO\textsubscript{2}, and Si\textsubscript{3}N\textsubscript{4}, are suitable and cost-effective pathways. The other limit of the application of ALD is the slowness in growth speed. One material at a time is deposited during one cycle with a deposition rate of 100–300 nm h\textsuperscript{-1} [58].

### 2.3. Subtractive manufacturing

Subtractive manufacturing has been widely adopted in the manufacturing process, in which the workpiece is formed by removing the amount of material to manufacture a workpiece with intricate surface/structure. In contrast to additive manufacturing, the break of atomic bonds is a key issue in atomic-scale subtractive manufacturing [60]. Nanoscale turning and milling, as the major UPM forms, are adapted from conventional subtractive manufacturing. In atomic-scale manufacturing, atomic force microscope nano-machining and chemical mechanical polishing are promising manufacturing methods of subtractive manufacturing, as those processes can reach surface roughness with angstrom dimensions.

#### 2.3.1. Ultra-precision machining

UPM refers to the process in which the undeformed chip thickness is at the close-to-atomic-scale level. The dimensional accuracy and surface roughness of the workpiece after UPM are less than 0.2 \( \mu \)m and 10 nm [61, 62], respectively. The precision of
the workpiece mainly depends on the relative motion accuracy between cutting edge and workpiece. Single crystal diamond tools with the nanometric tool edge are utilized in turning and milling processes to achieve UPM. The appropriate ultra-precision laths, diamond cutting tools, cutting fluids, and machining parameters are required to achieve the ultrahigh level of machining accuracy.

In close-to-atomic scale, the tool edge radius is an important parameter that cannot be ignored to affect the surface integrity. For the conventional cutting, the tool edge is considered to be sharp. However, for the ultra-precision cutting, the tool edge radius to be reckoned causes the effective rake angle to be negative, resulting in the compression of the workpiece surface [63], which leads to the material removal dominated by extrusion rather than material shear [64]. The extrusion with high hydrostatic pressure will change the lattice structure in the vicinity of the tool edge [65, 66], and hinder the formation of material defects [67]. The influence of tool edge radius on atomic-scale machinability of brittle materials, especially monocrystalline silicon, is very significant. With the significant effort of the researchers, currently, UPM has achieved a minimum chip thickness of 6 nm, and the surface roughness is close to 1 nm for monocrystal silicon [63, 68].

However, the achievement of atomic scale smooth surface of workpiece fabricated by UPM is still difficult. In particular, the removal of a single atomic layer of material by cutting tools has not been realized. The main reason is that the level of surface roughness is easily influenced by the machining factors, such as material property, tool geometry, tool wear and vibration. UPM requires a very small cutting depth, which is only a few atomic layers thick. The intermolecular interaction of the material and between materials, and the tool should be considered. The difference in the intermolecular interaction among different materials is one of the important reasons for the different optimal surface roughness. The surface roughness of silicon [69] and germanium [70] after UPM could reach the level of 10 nm, meanwhile the surface of steel and titanium alloy are hard to be mirror face by UPM. For crystal anisotropic single crystal materials, there are also significant differences in the cutting states along different crystal orientations [71].

MD can help researcher to elaborate of mechanism of some complex physical phenomena in the deformation region and the interface between the tool and surface in UPM. The deformation of atomic layer in the vicinity of the tool edge during material removal can be clearly described by MD under the effect of atomic sizing and tool edge radius effects [72]. Lennard–Jones potential is usually used as the potential function to describe the interaction between nonbonded atoms in MD simulation, which is far from enough in UPM because of the lack of description of covalent and metal bonds [73]. Other potential functions such as Morse, embedded atom method (EAM) and Tersoff are introduced into the MD simulation of UPM to describe the bonded interaction. Pei et al [74] compared the EAM and Morse potential in the UPM of copper cutting. In the MD model using two potentials, there is no obvious different of the chip and machined surface morphology. But the cutting force using Morse potential is much bigger than that using EAM potential. Pei et al found that EAM potential is more suitable for metallic bonding, which could be used for the simulation of metal cutting in UPM. Goel et al used MD to compare the difference between monocrystalline silicon and polycrystalline silicon in UPM, and described the process of brittle fracture, ductile plasticity, and structural changes of silicon in the cutting process [75]. Kim et al [76] compared the results of MD simulation and actual UPM experiment, as shown in figure 8(c). The position and size of the built-up edge and the shear plane were very similar, which showed...
that MD simulation could better describe the deformation of materials and the interaction between materials and tools in UPM. Goel et al. [77] studied the temperature distribution in the nano-cutting process of SiC. The maximum temperature in the deformation zone reached 1700 K. The high temperature led to the formation of SiC–graphene-like substance, which caused the ductile responses in the deformation zone. Although MD has been widely used in the simulation research of UPM, in many cases, there is still a lack of direct comparison between simulation results and experimental results under the same conditions. One of the important limitations is that in order to improve the calculation speed, the cutting speed is usually set to 500–1000 m s$^{-1}$, while the actual cutting speed may be only 1–2 m s$^{-1}$ or even lower.

2.3.2. Atomic force microscope nanomachining. The production of nanostructures is more difficult than that of atomic-scale smooth planes by UPM. Scanning probe lithography is an advanced subtractive manufacturing technology used to make nanostructures of the scale level of 10–100 nm [78–80]. Atomic force microscope is employed as the scanning probe lithography equipment to realize the ultra-precision nanostructures [81, 82]. The achievement of atomic-scale-depth material removal relies on hard tips, such as diamond [83] or Si$_3$N$_4$ [84], in an atomic force microscope to scratch on the material surface.

Some different methods have been proposed to attain the single atomic layer removal by AFM nanomachining, such as mechanochemical [3, 83] and electrochemical [85] methods. Chen et al. [3] proposed a tip-assisted, mask-less, and chemical-free nanolithography method, as illustrated in figure 9. They utilized micro-spherical AFM tip to achieve a single atomic layer removal. The removal mechanism can be attributed to a mechanochemical principle or tribochemistry process. The topset Silicon layer is removed by formation and then broken off the Si–O–Si bridge. This process, which involves the chemical bonding process, generally has a high energy barrier; however, the mechanical energy during the friction process decreases the critical energy barrier for the chemical reaction, which allows thermal activation at room temperature. It also determines the load-dependent removal efficiency.

2.3.3. Chemical mechanical polishing. Based on the similar mechanochemical principle, the CMP technology can enable an atomically flattened wafer surface with high material removal rate, and avoid surface damage, which is the basic procedure in integrated circuit (IC) manufacturing. Figure 10 illustrates the basic principle of CMP. The wafer and polishing pad move relative to each other by the load of carrier for polishing. Their contact surfaces are covered by a slurry mixed with chemical solutions and particles, which are used for mechanical polishing. The deposited film on the wafer surface is softened by a chemical reaction. The synergistic effect of the mechanical polishing of added silica abrasive and chemical erosion effect of polish liquid achieves the atomic-scale material removal of wafer surface [8, 86].

With the development of the IC techniques, chip integration is getting higher and the size is getting smaller, which advances the higher requirements on the process of CMP. Currently in 2021, the half pitch of Metal 1 has reached 5 nm. As the feature size of IC decreases, the uniformity of the wafer surface is required to be higher, to avoid the nonuniform lithography width. The extraordinary challenge of CMP is the global planarization across the larger-diameter wafer evolved from 8 to 12 inches. Prof. Lu has conducted a lot of works in CMP [8, 87, 88], and the industrial technology has also been generated. Meanwhile, the environmental issues in CMP process also needs extensive attention. Conventional CMP slurries consist of toxic or polluted ingredients, inducing
Figure 11. The mechanism of monolayer atom removal in CMP simulated by MD. (a) The sliding effect of silica cluster. Reprinted from [94], with the permission of AIP Publishing. (b) The impacting effect of silica cluster (with different impact speed). Reprinted from [95], with the permission of AIP Publishing. (c) The rolling effect of silica cluster. Reprinted from [96], with the permission of AIP Publishing. (d) The tribochemical wear in CMP. Reprinted from [28], Copyright (2017), with permission from Elsevier.

the pollution to the environment. To overcome this challenge, green CMP is developed for copper [89], sapphire [90], alloys [91] and diamond [92]. These works are a great contribution to the traditional CMP and manufacturing, effectively eliminating the pollution to the environment [90, 93].

MD was employed to describe the mechanism of atomic-scale material removal caused by the silica cluster, including extruding, sliding and rolling effect on the silicon wafer in CMP. The sliding effect of silica cluster on the substrate surface is the main removal mechanism. The results of MD simulation showed that the removal of monatomic layer can be achieved when the indentation depth is 0.1 nm [94]. Chen et al [95] studied the phenomenon of silica abrasive impacting the substrate. When the silica abrasive impact the substrate at a certain speed and angle, the atoms on the substrate surface are extruded under the combined action of impact phase transition, crystallographic slip, and thermal diffusion, as shown in figure 11(b). The MD model of abrasive rolling on the substrate was established by Si et al [96]. The silica abrasive is applied with a downforce and a lateral force to roll on the substrate. In the process of silica abrasive rolling, some atoms are adhered to the abrasive surface, so a small number of atoms are removed from the substrate surface.

The Stillinger–Weber-like potential [97] was the most common model employed to describe the Si and O mixed system in the mechanical force field of CMP process. The Stillinger–Weber-like potential models the stability order of silica polymorphs, and the radial distribution function of $\alpha$-SiO$_2$, which is suitable for the simulation of interactions of silica cluster-silicon wafer system. However, in most MD simulation researches, only mechanical effects were considered and chemical effects were ignored. The ReaxFF MD simulation was introduced by Wen et al [28, 98] to investigated the mechanism of tribochemical wear. The ReaxFF reactive force field can introduce the bond dissociation profiles to simulate the chemical reactive systems [99]. The ReaxFF MD results demonstrated the process of the single layer removal assisted by the chemical reaction, in which the formation of O–H bond decreases with the reaction barrier for Si–O–Si bond breaking, and the tensile stress assisted in breaking and removal. When the silica particle rolls across the silicon substrate some Si–O–Si bonds in the substrate surface breaks, dragging the Si atoms out and attaching to the abrasive particle.

Nanoscratching is a significant way to investigate the mechanisms of ACSM. Nevertheless, the speeds used in nanoscratching are at the speeds of $\mu$m s$^{-1}$ or mm s$^{-1}$, which is three to six orders magnitude lower than pragmatic CMP. To solve this challenge, a novel approach of single grain scratching was conducted at 40.2 m s$^{-1}$ and nanoscale depth of cut [100]. The speed employed in this research was four to seven orders magnitude higher than those used in traditional nanoscratching, which gave a new pathway to investigate the fundamental mechanisms of ACSM [100, 101]. Additionally, a crack is significant to keep the performance of a device, while it is difficult to explore the origin and evolution of a crack in a single crystal. Using the developed approach, a crack was found at the onset of crack, and the origin and evolution of a crack in a single crystal at atomic scale was interpreted by
MD simulations [102], as shown in figure 12. The simulation results were in good agreement between simulated and experimental results.

In addition to the polishing process, another important procedure is the cleaning. A direct cleaning method will leave a residue after liquid evaporation. One alternative method is based on the Marangoni effect during the wafer lifting process [103]. The meniscus flows down spontaneously with a little residue. Moreover, a cleaning medium can influence the cleaning by interfacial interactions between the abrasive and wafer across the medium [104].

2.3.4. Non-contact polishing. High precision mirror is necessary in extreme ultraviolet light (EUV) lithography equipment and synchrotron radiation, for the purpose of focusing, spectroscopy, and imaging. Considering the small wave length of the x-ray or EUV, the roughness of mirror is required to be smaller than 0.3 nm. Currently, ZEISS mirror productions, which is used in ASML NXE Lithography, reached a roughness of 0.1 nm [105]. In addition to mechanical polishing, several non-contact polishing methods have been proposed to prepare a smooth surface without damage.

The high precision of mirrors is generally achieved by a sequence of polishing procedures, and the last high-precision procedures include elastic emission machining (EEM) [107, 108], and IBE [109–111], which belongs to non-contact polishing. IBE is one of the applications of high energy ion beam.

3. External field assisted manufacturing

Generally, the atom scale or close-to-atomic scale manufacturing process requires a basic process of atom or molecule separating from the original site, or adding into a new site. This process can be conceptually seen as a transition of the target atom from one potential well to another with external mechanical interaction. This section will firstly go through the general models to describe it, and further propose potential method to improve the process.

3.1. Thermal activation models for manufacturing

The manufacturing process is usually accompanied with the destruction and reconstruction of chemical bonding (as well
as other kinds of interaction such as ionic bond, hydrogen bond, or van der Waals interaction) under the effect of external mechanical interaction. Thus, this process is equivalent to a mecanochemistry process, which can be theoretically described as a thermal activation model. Famous Eyring model to describe it was proposed in 1935 by Eyring and his co-workers, which was initially to calculate the absolute rates in chemical reactions based on transition state theory [112], and can be widely used to model the mechanism of viscosity, plasticity, and diffusion.

According to the thermal activation models, the potential function can be described as a Morse potential function [113]:

$$V(r) = D \left(1 - e^{-a(r-r_0)}\right)^2,$$

where \(r\) is the bond length, \(r_0\) is the equilibrium length, \(D\) is the activation energy supplied to break the bond. When the tension \(F\) is applied on it, the activation energy can decrease from \(D\) to \(D'\), which takes the form of

$$\frac{D'}{D} = x \log \frac{1 - x - \sqrt{1 - 2x}}{x} + \sqrt{1 - 2x},$$

where \(x = F/D\). In general, tension assists the chemical reaction, while the pressure force tends to oppose the reaction [114]. Figure 14 shows the mechanical force assisted thermal model. When considering the effect friction interaction, Briscoe et al proposed that the pressure stress \((P)\) can increase the barriers potential and the shear stress \((\tau)\) can reduce it, which takes the form of \(0 = k_B T \ln(v/v_0) + \langle Q + P\Omega - \tau \phi \rangle\) [115]. Here, \(Q\) is the initiate activation energy, and \(\Omega\) and \(\phi\) are activation volumes for pressure effect and shear effect, respectively, \(v\) is the moving velocity, and \(v_0\) is a characteristic velocity, \(k_B\) is the Boltzmann constant, \(T\) is the temperature.

Generally, the mechanism of manufacturing processes including atom transformation, subtractive manufacturing, and additive manufacturing introduced in section 2 can be conceptually summarized in the thermal activation model. That is, in the atom transformation or exchange process, the target atom requires an overcoming energy barrier to immigrate from the original bonding site to the AFM or STM tip site. This energy barrier comes from the bonding energy of the sample materials, which can be overcome by the external mechanical force or electrostatic force of the tunneling current. In the self-assembly process, the energy barrier (mainly comes from the electrical double layer force) is generally small and even vanishes because of the presence of strong attraction (such as van der Waals and hydrophobic forces). Thermal activation can drive the molecular assembly. In the subtractive manufacturing process, the atoms on the sample surface are required to be sequentially removed. This is achieved by inputting appropriate external energy to reduce the energy barrier of the target atoms. This external energy can be in the form of mechanical energy (pressure or shear) or ion beam.

For most manufacturing processes, external mechanical stress is the main source used to reduce the potential barrier. The single mechanical energy is limited and not very easy to qualitatively control. It can be expected that the external field energy, such as electrical energy, can be used to tune the energy barrier and assist the desired manufacturing process.

### 3.2. Electricity-assisted mechanical processing

In this section, we will theoretically discuss the influence of electricity, as well as the mechanical forces on the chemical reactions based on the thermodynamical model.

The discussions in the last section are based on the Gibbs free energy, which generally assumed that pressure force will retard the chemical process and the tensile stress will promote the process. This simple assumption is valid in many situations but is not always true. For example the transition of molecular hydrogen to semimetallic state can be achieved at pressure above 350 GPa [116]. Gutman [117] and Chen [118] suggested that concept of chemical potential, instead of Gibbs free energy, should be used in material science. Based on this concept, Liu et al [119] proposed their model for explaining the process of tribo-electrochemistry, which can be used to analyze the electricity-assisted manufacturing process.

Based on the concept of chemical potential, the generalized potential of mixture can be expressed as \(\mu = \mu_0 + RT \cdot \ln(a)\), where \(\mu_0\) is the chemical potential, \(R\) is the gas constant, and \(a\) is the activity. When electrical potential applied to the system, the electrochemical potential \(\mu_E\) can be expressed as \(\mu_E = \mu + zF\varphi = \mu_0 + RT \cdot \ln(a_E)\), where \(z\) is the ionic valence number, \(F\) is the Faraday’s constant, \(\varphi\) is the potential of the system, and \(a_E = a \cdot e^{zF\varphi}\) is defined as the electrochemical activity. When involving external mechanical force, the potential takes the form of \(\mu_j = \mu_0 + RT \cdot \ln(a_j)\), where \(a_j = a \cdot e^{\frac{zF\varphi}{RT}}\) is called tribochemical activity. Here, both the normal force and shear force is considered in the model as the pressure activation energy \((P\Omega)\) and shear force activation energy \((\tau \phi)\). Thus, the triboelectrochemical potential can be finally expressed as \(\mu_{BE} = \mu_0 + RT \cdot \ln(a_{BE})\), where \(a_{BE} = a \cdot e^{\frac{zF\varphi}{RT}}\). In general, external electrical field can equivalently adjust the reaction barrier of chemical reaction as the influence of external mechanical forces. More specifically, positive potential on the sample will promote the mecanochemical process, while the negative potential will retard the process. This provides...
additional dimensions to modulate the accuracy and efficiency of the mechanical manufacturing process.

Liu et al [119] designed a three-electrode friction system and verified the feasibility of theory. The important discovery is that the lubricated friction can be controlled by the applied elasticity. In the friction region, a colorful reaction layer (oxide layer) can be distinguished under moderate load and moderate electrical potential. The oxide layer will disappear when either friction stress or electricity was absent. This principle has the potential to achieve higher efficient and higher accuracy ACSM by applying it in the AFM system. Chen et al [120] used conductive AFM as a ‘scalpel’ for the layer-by-layer etching the oxide surface for 3D electrical characterization (shown in figure 15(a)). In their experiment, the etching scan was conducted with high stresses but with zero potential, while the reading scan was conducted with small stress with negative potential. Although the negative was applied mainly for electricity imaging, it meanwhile restarted the potential etching. Elena et al [121] presented the local oxidation nanolithography with a conductive AFM for the patterning of nano-metric motifs. In their experiment, the AFM tip did not contact with surface, which meant it was an electricity-dominated additive manufacturing process (shown in figure 15(b)).

Here, we can conclude the potential advantages and limitation for electricity-assisted mechanical manufacturing processing. The main advantage for electricity-assist is allowing for using smaller mechanical stress. Considering the AFM etching requires high contact stress and inevitably damage probe, the small mechanical stress can efficiently protect the AFM tip and increase the stability of manufacturing. The other advantage can potentially increase the output efficiency as long as the accuracy can be guaranteed. The third advantage is that it provides additional dimension to regulate. The typical example is that by applying positive potential on the sample, the oxidation process may induce an additive manufacturing process, or we may call it a nano-scale 3D printing. The main disadvantage for electricity-assisted mechanical manufacturing processing is the limitation for sample material. It generally worked well for thin insulation material on conductive substrate or semiconducting material, and the materials also cannot be electrochemically inert. Metallic material seems to be appropriate materials, however the manufacturing accuracy control may become difficult, because the lateral resistance is small and the region of electrical influence may be enlarged.

4. Conclusion and perspective

Manufacturing is the cornerstone of the advancement of human civilization. In today’s information age, various types of chips shape the people’s convenient life and advanced industry. Advanced computer microprocessors have stepped in to the manufacturing process of the 3 or 2 nm node, which generally means a high computational efficiency and low energy consumption. However, such a small scale is equivalent to only several tens of atoms, and will introduce huge difficulties for precise, efficient, and large area fabrication in IC manufacturing. The increasing research of ACSM provides fundamental insights on the mechanism of the atom-scale science, and advanced techniques to deal with the challenge in atomic scale manufacturing.

At atomic and close-to-atomic scale, the theoretical mechanism cannot be attributed to macroscale mechanical...
principles, such as shearing, extruding, or rubbing. Intermolecular and surface forces (essentially quantum theory) at atomic and close-to-atomic levels need to be considered, as well as the thermal dynamic model as a general treatment. Therefore, the further development of ACSM faces great challenges. At present, researchers have not established an accurate and efficient model to accurately describe the behavior of atomic motion and interaction in ACSM. The machining accuracy determined by quantum mechanics and intermolecular force leads to the removal or increase of monatomic layer from substrate surface is very difficult.

In order to solve the difficulties of further development of ACSM in the future, we need to clearly explain the role of intermolecular force in ACSM. The widely existing intermolecular interactions or intramolecular interaction determines the properties of matter, and the physical and chemical behaviors in atomic-scale manufacturing. Understanding and using intermolecular and surface forces are the basis for better designing and performing atomic-scale manufacturing. This review analyzed how intermolecular forces participated in the atom transformation by STM or AFM, self-assemble, AFM-based nanomachining and chemical mechanical polishing. A general stress-assisted thermal activation model was used to explain the migration of surface atoms. Currently, several interesting multiphysics effects have garnered significant attention, such as mechano-chemistry [122], mechano-luminescence [123], electro-mechanical [124] and mechanical-thermal [125]. Combined with the multiphysics fields including the electrical, laser, or temperature fields, similar with the mechanochemical, it is expected to achieve high-efficiency atoms removal and make high-accuracy fabrication.

However, researchers need to realize that some ACSM methods relying on STM and AFM in laboratories, which use intermolecular forces to complete atomic scale transfer, cannot achieve large-scale efficient industrial applications in the foreseeable future. In addition, like the chip industry represented by CMP, atomic manufacturing accuracy can be achieved, but the cost of resources and money is still very high. From a long-term perspective, we need to promote Manufacturing III represented by ACSM to be as convenient, steady and efficient as Manufacturing II. This goal depends on the further maturity of the application of quantum mechanics and intermolecular force theory in ACSM, also on the further development of materials, manufacturing tools, and ultra-precision measurement technology. In basic theory of ACSM, we need to establish the universal atomic scale theoretical model for the existing high-efficiency ACSM process, such as UPM, to further improve its applicability in atomic scales and more materials, or explore more representative ACSM methods utilizing intermolecular force.

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