Response of ultrathin metal films to ultrafast laser irradiation: A comparative molecular-dynamics study

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Abstract.
Using molecular-dynamics computer simulation, we study the materials processes in ultrathin metal films induced by ultrafast laser irradiation. We investigate four different metals (Al, Cu, Ti, W), which vary widely in their cohesive energy, melting temperature, bulk modulus, and crystal structure. Despite these variations, we find that the same materials processes are induced in these films: With increasing laser fluence, the film melts, voids are formed, the film tears (spallation), and finally fragments to form a multitude of clusters. When the energy transfer starting the process is scaled to the cohesive energy of the material, the thresholds of these processes adopt similar – but not identical – values.

1. Introduction
Laser irradiation of metals may lead to an interesting variety of materials phenomena, including melting, boiling (phase explosion), spallation, vapor formation, etc. [1]. Due to the non-equilibrium nature of these processes, atomistic simulations of the phenomena occurring have been attempted in the recent past using molecular-dynamics simulations [2–13]. Such an approach is particularly useful for ultrashort laser irradiation (fs- or ps-laser pulses). Such ultrashort laser pulses have found widespread application in areas such as surface melting, ablation, hole drilling, etc. [1].

In the present paper we wish to explore the processes that are induced in various metals under ultrashort laser pulses using molecular-dynamics simulation. To this end we focus on the influence of different materials parameters by studying in parallel the effects induced in 4 different metals, Al, Cu, Ti, and W. For simplification, we study the laser irradiation of ultrathin free-standing films. Their width is chosen so narrow that ballistic electrons distribute their energy more or less homogeneously throughout the film. Thus, the electronic energy can be assumed to be homogeneous throughout the film. As a further simplification, we model the laser irradiation to be instantaneous, i.e., the laser energy is given to the atoms immediately at the start of the simulation. While in the simulation of any real experiment, the finite laser pulse width and the electron-phonon relaxation time will delay and smoothen the energy transfer from the electronic to the atomic system, in this investigation we will not consider this effect.
Table 1. Materials properties (experimental values) of the four metals studied. $E_{coh}$ cohesive energy, $B$ bulk modulus, $n$ atomic number density, $M$ atomic mass, $T_m$ melting temperature, $T_b$ boiling temperature at 0.1 MPa pressure, $T_c$ critical temperature.

| metal   | $E_{coh}$ (eV) | $B$ (GPa) | $n$ (nm$^{-3}$) | $M$ (amu) | $T_m$ (K) | $T_b$ (K) | $T_c$ (K) |
|---------|----------------|-----------|-----------------|-----------|-----------|-----------|-----------|
| Al (fcc)| 3.39           | 72.2      | 60.2            | 27.0      | 933       | 2623      | 5410      |
| Cu (fcc)| 3.49           | 137       | 84.5            | 63.5      | 1356      | 2853      | 5890      |
| Ti (hcp)| 4.85           | 105       | 56.6            | 47.9      | 1933      | 3560      | 7890      |
| W (bcc )| 8.90           | 323       | 63.0            | 183.9     | 3683      | 5933      | 13890     |

1Ref. [18].  2Ref. [19].  3Ref. [20].

2. System

In our simulations, the films have a thickness of 20 ML, and a lateral cross section of $20 \times 20$ ML. Laterally, periodic boundary conditions are employed, while the top and bottom surfaces are free. For the fcc (hcp, bcc) crystallite, the top and bottom surfaces have a (100) [(1000), (100)] crystallography, and the total number of atoms in our simulation cell amounts to 4000 (2000, 2000) atoms. At time $t = 0$, the film is energized by giving each atom a kinetic energy $E_0$. In the simulation this is accomplished by assigning each atom a velocity $\sqrt{2E_0/M}$ in random direction, where $M$ is the atom mass. The simulations have been followed until up to 30 ps after irradiation.

In the following, we shall call the energy $E_0$ imparted at time $t = 0$ to each atom the energy transfer or ‘energization’. In our model, it is the sole characteristics of the laser irradiation which enters the model. It is connected to the absorbed laser fluence $\Phi$ via the thin film width $L$ and the atomic number density $n$ through

$$\Phi = E_0Ln.$$  \hspace{1cm} (1)

We study four different metals: Al, Cu, Ti, W, with film thickness $L = 40.3 \ (36.1, 44.5, 31.6)$ Å, resp. Several experimentally determined properties of these materials are assembled in Table 1. The interatomic potentials employed in the simulation of these metals are the many-body potentials of Ref. [14] for Cu, Ref. [15] for Al, and Ref. [16] for Ti and W, resp. We note that these potentials have been designed such as to correctly reproduce the ground-state crystal structure, the cohesive energy $E_{coh}$ and the bulk modulus $B$ of these materials. Furthermore, the Al potential also reproduces the melting temperature [15]; the Cu potential features a by 13 % too high melting temperature [17], while the melting temperature exhibited by the Ti and W potentials have not been determined to our knowledge. Also the boiling temperatures $T_b$ and critical temperatures $T_c$ corresponding to the four potentials are not known.

We note that the metals will also differ strongly in the properties of their electronic systems, such as the electronic heat capacity and diffusion coefficient, and furthermore in the laser penetration depth and the electron-phonon-coupling time. These properties are not considered in the present paper; due to the assumption of a sudden energy transfer, we focus on the materials properties of the metals. The influence of the electronic materials properties would be conveniently performed in terms of the two-temperature model [21] and has been reported elsewhere [22, 23].

Temperature and pressure in the film are measured as averages over the central third part of the film. Note that these quantities are not uniform in the film [4, 9, 17]. In particular, the pressure shows an inhomogeneity since it vanishes at the free surfaces.
Figure 1. Series of snapshots of the energized Al film featuring the materials processes investigated. All figures taken at 5 ps after energization to $E_0$. Color denotes the local temperature in Kelvin. a: Crystalline. b: Molten c: Temporary void formation d: Spallation e: Cluster formation.

3. Results

Fig. 1 exemplifies the materials processes occurring in the thin film after irradiation for the case of an Al target. We find definite thresholds for the energization $E_0$, above which a new process in the thin film is initiated:

(i) At small energizations, the crystalline film is heated up, but does not melt.

(ii) After a threshold, $E_0 = 0.3$ eV, the film melts. In the case of the fcc crystals melting is monitored with the help of the local-order parameter as given in Refs. [9, 24], and in the case of the hcp and bcc crystals by visual inspection.

(iii) Beyond an energization of $E_0 = 0.6$ eV, voids form in the film. The formation of these voids is due to a universal mechanism: Due to the sudden energy transfer, the film reaches a high compressive pressure and accordingly expands. This expansion eventually induces a tensile pressure in the material. In the liquid state, the molten metal cannot sustain large tensile
pressures, and accordingly voids are formed. If the tensile pressure is small, the voids will collapse again.

(iv) With increasing energization, \( E_0 > 0.8 \text{ eV} \), the voids formed will not collapse but induce the tearing (spallation) of the entire film. While the term ‘spallation’ is often reserved for the break-up of a solid, we shall use this term also in our case, where this process occurs in the liquid phase. The liquid cannot sustain the strong tensile pressure, which builds up, and hence tears.

(v) At even higher energization, \( E_0 > 1.2 \text{ eV} \), multiple spallation processes will occur, and also evaporation of atoms will start, resulting in the complete fragmentation of the film into a multitude of clusters of various sizes. While the detailed shape of the cluster distribution depends on the initial energization [25], we assume the cluster formation process to have started when the film has fragmented within 10 ps into at least three fragments. With higher energization, the number of fragments formed increases while their average size decreases.

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**Figure 2.** Synopsis of energization thresholds, \( \epsilon = E_0/E_{coh} \) for the four metals studied.

We found the same sequence of events occurring also in the other materials studied, but with different thresholds of energization. In Fig. 2, a synopsis of the energy thresholds for the five processes discussed above for the metals studied is presented. For this comparison, the energization is given in reduced units

\[
\epsilon = \frac{E_0}{E_{coh}}
\]

with the idea, that it is the cohesive energy, or bond strength, which dominates the relevant energy scale in the material. Fig. 2 shows that in fact the two fcc materials, Cu and Al, show very similar energization thresholds; an exception is the threshold to cluster formation, which occurs earlier in Al. The two other materials need considerably stronger energization for the processes to occur. As an example, spallation only occurs for \( \epsilon > 0.37 \) in Ti, while it already occurs at \( \epsilon = 0.28 \) in Cu. This feature may be related to the different crystal structures of Ti and W.

Table 2 summarizes several relevant parameters of the melting, the void formation and the spallation process obtained from our simulations. We see that at the melting threshold, the
Table 2. Characteristics of the melting, void nucleation and spallation processes studied, for an energization at the process threshold. 
\( \epsilon = E_0/E_{\text{coh}} \) energization threshold.

\( t \): time for completion of process. In the case of void nucleation and spallation, the times for both the beginning and the completion of the process have been indicated.

\( T (p) \): Temperature (pressure) averaged over the central third part of the film at time \( t \) (i.e., at completion of melting, but at the beginning of void nucleation and spallation).

| metal | melting | | void nucleation | | spallation |
|-------|---------|---|---------|---|---------|
|       | \( \epsilon \) | \( t_m \) (ps) | \( T \) (K) | \( p \) (GPa) | \( \epsilon \) | \( t_{\text{void}} \) (ps) | \( T \) (K) | \( p \) (GPa) | \( \epsilon \) | \( t_{\text{spall}} \) (ps) | \( T \) (K) | \( p \) (GPa) |
| Al    | 0.11    | 1.4 | 952    | -1.76 | 0.20    | 1.4 - 3.6 | 1689    | -2.48 | 0.26    | 1.2 - 4.0 | 2061    | -2.13  |
| Cu    | 0.14    | 1.9 | 1312   | -1.73 | 0.20    | 1.9 - 3.0 | 1381    | -4.01 | 0.28    | 1.7 - 4.7 | 1878    | -2.77  |
| Ti    | 0.16    | 1.5 | 1501   | -3.75 | 0.28    | 1.5 - 4.0 | 2277    | -4.18 | 0.37    | 1.3 - 4.8 | 2848    | -3.53  |
| W     | 0.18    | 22.0| 4049   | -1.53 | 0.30    | 1.8 - 5.0 | 5976    | -5.55 | 0.37    | 1.4 - 11.7 | 6825    | -5.94  |

The melting process itself occurs very fast, in the order of 1.4 – 2.0 ps. The temperature reached in the film when melting nominally occurs is exactly at the melting temperature.

At the spallation threshold, the pressure reached on average in the film is tensile, \( p < 0 \). In all four materials, it is of the order of 2% of the bulk modulus. Spallation occurs very quickly; voids start forming at 1 ps after irradiation, and the spallation process is complete after 12 ps.

At energizations below the melting threshold, the crystal heats up strongly, but remains crystalline. In Fig. 3 we show cross sections through the heated crystal at an energization of 95% of the melting threshold. While the crystalline structure is still intact, small defects are visible. The amount of crystalline disorder changes considerably between the 4 metals studied. Thus, while the Al crystal structure appears virtually undamaged, small pockets are seen in Cu, which appear already to be highly disordered or even partly molten. The W and Ti structures appear to be disordered not only locally, but throughout the cross section shown here. Note, however, that even after following the simulation to 30 ps, these crystals do not melt. We note
Figure 3. Snap shots of the four metals at an energization of 95 % of the threshold to melting, at a time of 5 ps after energization. The cross sections shown are 5 ML deep. Color denotes the local temperature, as in Fig. 1. While all four metals are crystalline, they show a varying degree of disorder.

Furthermore that in the case of brittle materials, such as Cr or Ti, it is well known that under ns-laser irradiation with intensities below the melting threshold, cracks are formed [26, 27]. We did not observe this process to happen in our simulation, probably due to the small size of our simulation volume.

4. Conclusions
We studied the response of four different metals with widely varying properties to a sudden energy transfer, such as that which might be induced by ultrafast laser irradiation. With increasing energization, we find the same sequence of events occurring in the metals: melting, void formation, tearing of the solid (spallation), and fragmentation to a cluster cloud. The thresholds for these various processes have been identified for the four materials studied. Upon scaling the threshold energizations to the cohesive energy of the metals, the thresholds attain similar values for the two fcc metals, but somewhat higher values for Ti and W.

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