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Self-limit in glaser crystallization and direct writing of 2D materials

[1]pradyumna Kumar Pradhan, [2]soubhagini Mandal,
Gandhi Institute of Excellent Technocrats, Bhubaneswar, India
Black Diamond College of Engineering & Technology, Jharsuguda, Odisha, India

ABSTRACT:
Direct growth and patterning of atomically thin two-dimensional (2D) materials on varioussubstrates are essential steps towards enabling their potential for use in the next generation ofelectronicandoptoelectronicdevices.Theconventionalgas-phasegrowthtechniques,however,
are not compatible with direct patterning processes. Similarly, the condensed-phase methods,basedonmetaloxidedepositionandchalcogenizationprocesses,requirelengthyprocessingtimesandhightemperatures.Here,anovelself-limitinglasercrystallizationprocessfordirectcrystallization and patterning of 2D materials is demonstrated. It takes advantage of significantdifferencesbetweentheopticalpropertiesoftheamorphousandcrystallinephases.Pulsedlaserdepositionis used todeposita thin layerofstoichiometric amorphous molybdenum disulfide (MoS_2)film(~3nm)ontothefusedsilicasubstrates.Atunablenanosecondinfrared(IR)laser(1064nm)isthenemployedtocoupleapreciseamountofpowerandnumberofpulsesintotheamorphousmaterials forcontrolled crystallizationanddirectwritingprocesses.TheIRlaser interactionwiththeamorphouslayerresultsinfastheating,crystallization,and/orevaporationofthematerialswithinanarrowprocessingwindow.However,reductionofthemidgapanddefectstates in the as crystallized layers decreases the laser coupling efficiency leading to higher tolerancetoprocessparameters.Thedeliberatedesignofsuchlaser2Dmaterialinteractionsallowstheself-limitingcrystallizationphenomenatooccurwithincreasedqualityandamuchbroaderprocessingwindow.Thisuniquelaserprocessingapproachallowshigh-qualitycrystallization,directwriting,patterning,andtheintegrationofvarious2Dmaterialsintofuturefunctionaldevices.
Keywords:2Dmaterials,directlaserwriting,lasercrystallization
(Somefiguresmayappearincolouronlyintheonlinejournal)

INTRODUCTION

Therecentdiscoveryofatomicallythintwo-dimensional(2D)materials has revealed promising potential for advancing thefutureofoptoelectronics,photonics,sensing,andenergyapplications[1–19].Inparticular,mono-andfew-layertrans-itionmetaldichalcogenides(TMDCs)withageneral formulaofMX_2(whereM=Mo,W,etc;X=S,Te,Se)have attractedsignificantresearchattentionmotivatedprimarilybytheirexcitingelectronic,optical,andphotonicpropertiesinthevisible and near-infrared part of the spectrum [20–23]. Forinstance, some of these materials (e.g. WS_2, MoS_2, $MoSe_2$,WSe_2) transition from an indirect to direct [24, 25] bandgap astheyreachasingle-layerlimit.Duetotheirreducedscreening
of Coulomb interactions, TMDCs exhibit strong many-bodyinteractions which result in strong binding of excitons, biex-citons [26], and trions [27]. Broken inversion symmetry andstrong spin–orbit coupling [28] can also open the possibility fornonlinearlight–matterinteractions,includingsecondharmonicgenerationinthesematerials.

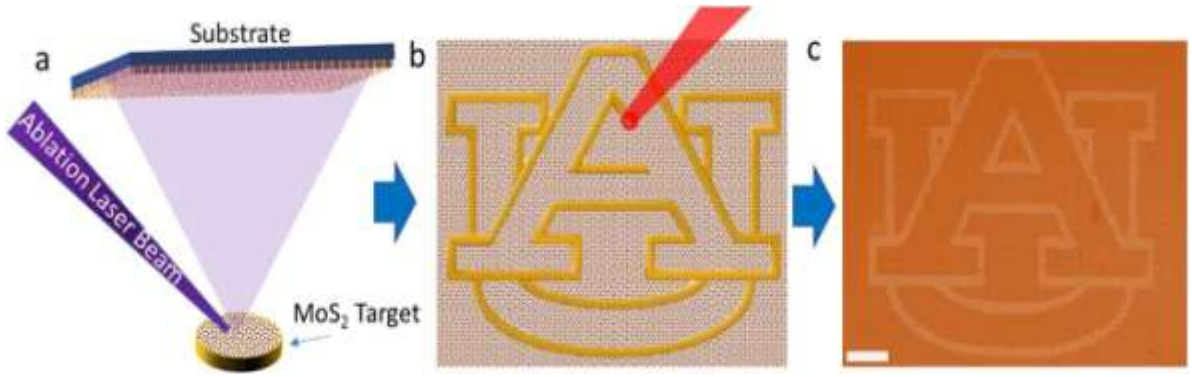

Figure1.Schematicrepresentationsoftheexperimentaldesignandprocessflow.Pulsedlaserdeposition(a)andlaserwriting/crystallizationsetups (b) were used for deposition of amorphous thin films and crystallization/writing of 2D materials, respectively. The optical image (c)showsarepresentativelaser-crystallizedMoS_2pattern(AuburnUniversitylogo)onthefusedsilicasubstrate.Thebrightlinesanddarkbackgroundindicatethecrystallineandamorphousregions,respectively.Thescalebaris200μm.

Asignificantamountofresearchinteresthasbeendevoted to scalable, tunable, and defect-free synthesis andprocessing of TMDCs [29–35]. Many synthesis techniques,includingchemicalvapordeposition[36],metalorganic chemical vapor deposition [37], and molecular beam epitaxy(MBE) [38], have been developed to control the growth ofsuchmaterialsonvarioussubstrates.Despitesignificant progress in the growth of a few 2D TMDCs using thesetechniques, they have major disadvantages when it comes todeviceintegrationandpatterningflexibility.Forinstance,very high substrate temperatures (e.g. 850 °C) in the above-mentionedgrowthmethodssignificantlylimittheircompatibility with flexible or traditional semiconductor patterningand device integration technologies (e.g. photolithography).In order to overcome these major issues, novel synthesis andprocessingapproachesarerequired.

Here, a laser-based synthesis and processing method isreportedthatreliesonself-limitinglasercrystallization(SLLC) ofstoichiometricamorphousthinfilms(~3–5 nm)depositedontofusedsilicasubstratesviapulsedlaser deposition (PLD) of a MoS_2 target. This technique mainlytakes advantage of significant contrasts between the opticalpropertiesoftheamorphousandcrystallineMoS_2phases. MoS_2waschosenasthematerialofinterestduetoitsfascicrystallizationprocesswithnofurthereffectontheirradiated/crystallized materials leading to a higher tolerance to processparameters, better crystallinity, and a much broader processwindow.

1. Experimental design

Figure 1shows the schematics of our laser synthesis andprocessing approaches with a representative optical imageshowing a laser-crystallized, few-layer MoS_2 film on a fusedsilicasubstrate.Inthisprocess,wefirstdepositedathinfilm ofstoichiometricamorphous2DTMDCsontothefusedsilicasubstrates due to their high transparency at near-infrared (IR)(i.e. 1064 nm) wavelengths. This allowed us to minimize thelaserinteractionwiththesubstrateduringthecrystallization process. PLD [33, 39, 40] was used as a versatile method ofdepositing a stoichiometric layer of MoS_2 thin film onto thesubstratesatroomtemperature.A1inchdiameterMoS_2targetwasplacedonatargetcarouselinsideasphericalchamber (21 inches in diameter). An excimer laser (COMPexPro®,KrF248 nm,20ns)wasusedtoablatetheMoS2targetata40°angleofincidenceand2Hzrepetitionrate.Theresultant laserspotsizeandfluenceonthetargetwere2×5mmand

nating optoelectronic properties and the existence of a largeamountofavailabledataforvalidationoftheresults.

In general, a monolayer MoS_2 crystal is a direct bandgapofan~2 eV(620 nm) semiconductor[24].However,whenthefilmthicknessismorethanfivelayers,MoS_2behaveslike anindirectbandgapsemiconductorwithasmallerbandgap

1.3 eV (~950 nm) [24]. We show that a large number of thedefect,imperfection,andmidgapstatesintheamorphous materials enhance the absorption at below bandgap energies.Thecontrolledirradiationofsuchamorphousmaterialswithatunable nanosecond 1064 nm laser offers multiple advantagesby:(1) efficientlycouplingintotheamorphousfilmtoselectively heat the materials, rearrange the atoms, and crys-tallizethefilms;(2)subsequentlyreducingthedefectsstate andrecoveringthebandgaptoitscrystallineform;and
(3)reducingthecouplingefficiencyandself-limitingthe
1.5 J cm^{-2}, respectively. The vacuum chamber was pumpeddown to 5×10^{-6}Torr for deposition, and the substrate-to-targetdistancewassetat13cm.Thenumberofdeposition
pulses was kept at 200 for all of the depositions described inthispaperforconsistency.
After deposition of the amorphous MoS_2 thin films ontothe fused silica substrates, we transferred the samples to ahome-builtenvironmentalchamberforlaserprocessingthrough a quartz window. The SLLC process and laser writ-ing experiments were performed in an argon environment atatmospheric pressure and room temperature. The chamberwas first flushed with argon gas for a few minutes to ensuretheremovalofpossibleoxygenresiduesfollowedbya100 sccmflowratetopreventairfromentering intothechamber. Samples were then controllably crystallized by a130Wtunablenanosecondlasercapableofemitting

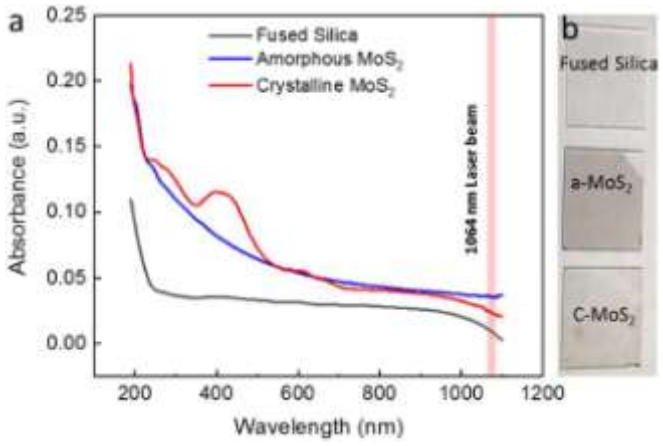

Figure 2.Absorption spectra (a) of fused silica (black), amorphous(blue), and crystalline (red) MoS_2 thin film. The spectra were takenfrom the samples in (b), as labeled. The crystallized sample showsabsorptionpeaksat680,620,and450nmsimilartothefew-layer
MoS_2 crystal [24]. The amorphous film shows higher absorption at1064nmthanitscrystallinecounterpart.

nanosecondpulses(5–2000nsin63waveforms)withapulseenergyfrom0.04to1.57
mJandarepetitionraterangingfrom1Hzto4160KHz.Thelaserbeamwascoupledintoa
galvo scanner with a 10 μm focal point and a scan speedranging from 1 to 5000 mm s^{-1}. A laser marking software(Laser Studio Professional) was used to design various pat-terns and control the process parameters (e.g. power, pulseduration, number of pulses, scan speed, repetition rate) foreachspecificpattern.Wedesigned5×5dotmatriceswitha
100 μmdistancebetweenthedotsthroughouttheexperi-ments. The pulse width and repetition rate of the laser werekept constant at 261 ns and 1 MHz, respectively, in all of theexperiments.

2. Resultsanddiscussions

ToestablishtheSLLCconcept,wefirststudiedtheabsorptionbehavior of the MoS_2 thin films deposited, both before andafter the crystallization process. According to the absorptionspectra shown in figure 2, the crystallized MoS_2 samplesdevelopedclearpeaksat680and620 nmsimilartotheabsorption peaks of mono- and few-layer MoS_2 crystals [24].TheabsorptionspectrumofamorphousMoS2thinfilm,onthe
other hand, did not show any identifiable peak. However, theamorphous film showed higher absorption at near-

IR (e.g.1064 nm), nearly twice as large as its crystalline counterpart.ThelackofdistinctabsorptionpeaksinamorphousMoS_2 films can be attributed to a large number of defect, imper-fection, and midgap states [41] in the material that are alsoresponsible for their enhanced absorption at below bandgapwavelengths.

Takingtheopticalabsorptiondataintoconsideration,westudied the interaction of a 1064 nm tunable nanosecond laserbeamwiththeamorphousMoS_2film.Wefoundthatthelaserinteraction with the amorphous material often resulted in theevaporationofthe2Dmaterialwithaverynarrowchoiceof power and pulse numbers for crystallization. In the SLLCprocess, the crystallization was initiated at a low laser irra-diation power (below the initial damage threshold); and oncetheamorphousMoS_2filmstartedtocrystallize,thelightinteractionwiththematerialbecameweakerduetothe reductionofmidgapanddefectstatesinthecrystallizedstructures.Thisinitialcrystallizationandreductioninmidgapstate s enabled us to significantly extend the laser power andpulse number far beyond the damage threshold to furtherimprovethecrystallizationqualitywithoutdamagingtheMoS_2layers.

In order to study the crystallization dynamics and iden-tifythedamagethresholds,weperformedasystematicexperimental study to find all of the possible noninteracting,crystallizing,anddamagingzonesasafunctionoflaserpower (from65to130W)andthenumberofpulses(from2to50).Figures3(a)–(d)showtheopticalimagesofasetofpatterns,on~3nmthick,PLD-depositedamorphousMoS_2filmscreatedbyvariouslaserparameters,asindicatedonthe images. We performed a comprehensive experimental studyto find how the material responds to the process parameters.Weobservedthattheamorphousmaterialwaseitherunchanged,crystallized,orevaporated,dependingonth elaserpowerandthenumberofincidentpulses.Generally,theeffectoflaserpowerandnumberofpulseswasobservedtobe inverselyproportional,i.e.increasingthelaserpowerrequiredthenumberofpulsestobedecreasedtoinducethesameeffec t on the films. Figure 3(e) shows the heatmap of the zonesexperimentallyobtainedinthisstudy.Itwasobservedthatthecrystallizationzone(red),wherethebestqualitycrysta lsform,wasverynarrow.Abovethisredzone,materialdamage(pink) and evaporation (white) occurred; and below it, crys-tallization quality faded (yellow) or no effect (blue) took placeatall.Asisapparentfromthenarrowcrystallizationwindow, high laser powers evaporated the materials due to the stronginteraction with the amorphous film. To probe the structuralevolutionoftheMoS_2filmineachzone,weperformeda Ramanstudy,asshowninfigure3(f).TheRamanspectraandmapswere acquiredusing a532 nm laser excitationsource,50xobjectivelens,and1200lmm^{-1}grating.TheRamanspectra of amorphous films (Line 1) showed a broad shapewithnovisiblepeaks.TheMoS_2Ramanfingerprintsat 375and 403 cm^{-1}startedappearing(Line2) andgettingstronger(Lines3and4)forhigherlaserpowersornumberofpulses in the crystallization zone. Finally, the MoS_2 Ramanpeaks started disappearing (Line 5) as the process parametersenteredtheevaporationzone.Suchanarrowcrystallization zone limited the MoS_2 tolerance to even a small variation intheprocessparameters.

In principle, when the amorphous material is irradiatedwith a laser pulse, its temperature rises instantly. At hightransient temperatures, the material gets close to its meltingpoint which possesses different optical properties than at itscrystalline phase. Therefore, further addition of energy intothe system drives the material into the evaporation zone. Toimpose an SLLC condition, it is essential to design a multi-step processing sequence. We mainly started the SLLC pro-cessfromasafeprocessingzonewherethecrystallizationhad

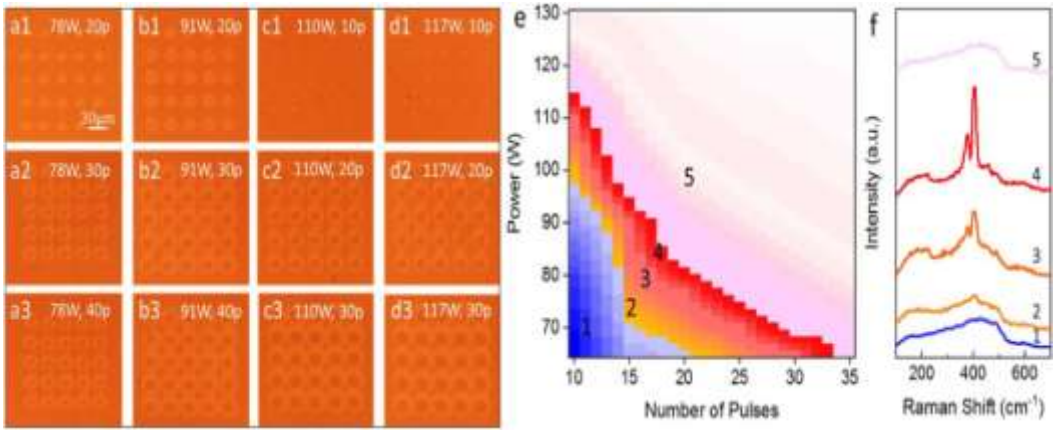

Figure3.Representativeopticalimages(a)–(d)andcomprehensiveheatmap(e)ofthematerial'sresponsetodifferentlaserpowersandnumberofpulses.Blue,red,and pinkzonesaretheprocessregionswherenoeffect,crystallization,ordamageoccurred,respectively.TheCorrespondingRamanspectra(f)showthestructuralevolutionofthefilmsineachregion,aslabeled.

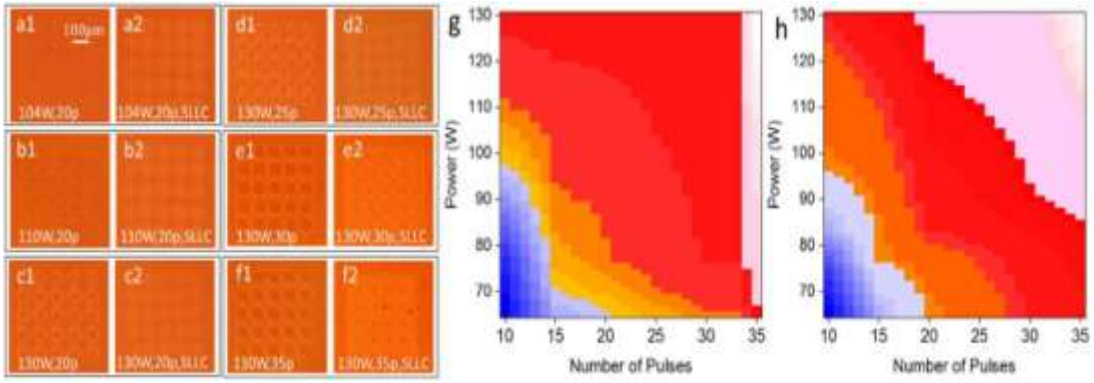

Figure4.Representativeopticalimages(a)–(f)showingthelaserinteractioneffectsontheamorphousMoS_2filmwithandwithouttheSLLCconceptaslabeled.Samplesprepareusing theSLLCapproachwereallcrystallizedwithoutanyvisibledamage,whilealloftheirnormallyprocessedcounterpartsevaporated.Asshown,theself-limitingprocesscanextendthesafecrystallizationzoneupto100%laserpowerwithoutdamage.Heatmapsshowthebroadcrystallizationzones(red)byeithersequentialpowersweep(g)orsequentialpulsenumbersweep (h)duringthecrystallizationprocess.

just been initiated (defined in figure 3(b)), followed by asequentialincreaseintheprocessparameters(i.e.laserpowerand/or pulse number) with a few milliseconds delay timebetweentheprocesssteps,allowingfasttemperature
quenching and crystal formation. This guided the material toits crystalline phase in each laser treatment, before pumpingmoreenergyintothematerialsystem.

Figures 4(a)–(f) show the representative optical imagesofMoS_2thinfilmprocessedwithandwithouttheSLLC method. The images with a 1 following a letter represent theeffectoflaserpowerandthenumberofpulsesthatresultedinsignificant damage and evaporation in the normal laser pro-cessing approach, as indicated in figure 3. The images with a2 following a letter show the perfectly crystallized samplesprepared by the self-limiting process with no damage at all.Forexample,whilethe104 Wlaserpowerwith20pulses
(figure 4(a1)) significantly damaged the film in the normalprocess, the SLLC approach did not damage the film even at130 W(figure4(f2)) wherethelaserpowerwasincreasedfrom65to130Wwitha1 Wincrementinlaserpowerand35 pulses in each step. To investigate this effect further, weperformed a large set of experiments to identify noninteracting, crystallizing, and damaging process parameterzonesinthissequentialself-limitingprocess.Heatmapsofthematerial'sresponsetosequentialpower(figure4(g))and pulsenumberincreases(figure4(h))wereplottedtovisualize
theresultingbroadcrystallizationzones(red)inthisprocess.

Forsequentialsweepingofpower,thelaserpowerwasincreasedstartingfrom65 Wtothedesiredpowerin1 Wincremental steps and a few milliseconds delay time betweenthe steps, with a constant number of pulses in each step.

Forsequentialsweepingofthepulsenumber,the numberof pulseswasincreasedfrom5tom5(wheremrangesfrom1to10)withafewmilliseconds delaytimebetweenthestepsandaconstantpower ateachstep.Theblue coloronthe heatmap represents the unaffected zone, while the pink to white colorindicatesthedecompositionand/orevaporationzones.Itis evident from the heatmaps in figures 4(g) and (h) that betterandbroadercrystallizationzones(red)occurredinthismethod.ThisSLLCmethodsignificantlyincreasedthepro-cess window as well as the quality of the MoS_2 crystals sincethe laser interacted with a 'crystalline' phase in each step(afterthefirsttreatment).Futuremodelingandtheoretical

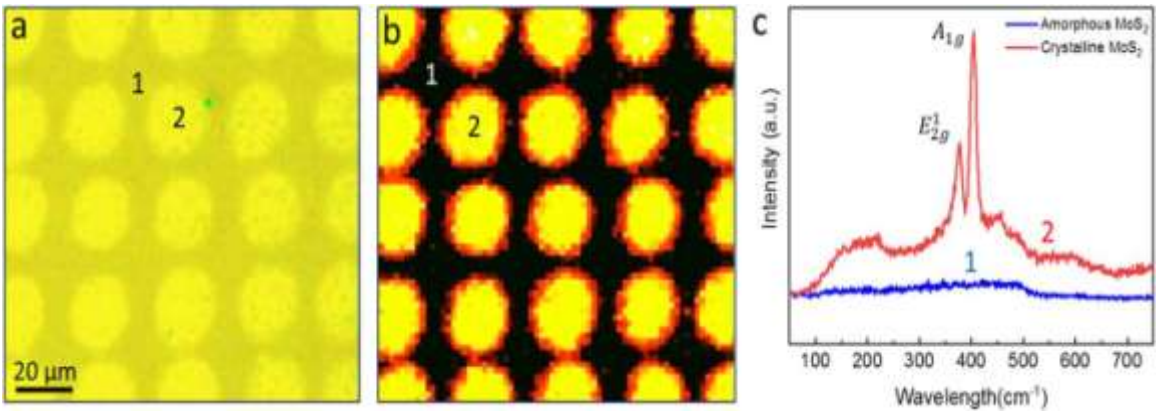

Figure5. Anopticalimage(a)andaRamanmap(b)ofacrystallizedMoS_2matrixshowingthespatialuniformityofthecrystallize dregions.Thesamplewaspreparedinan SLLCapproachbyswipingthepowerfrom60to91Wwith1Wpowerincrementan d30pulsesineachstep.Ramanspectra(c)obtainedfromtheamorphousandcrystallizedregionsaslabeledontheimages.T heamorphousspectrumdoesnothaveanyidentifiableMoS_2fingerprintswhilethecrystallizedpartshowstwointensepea ksat375and403cm^{-1}correspondingtocrystallineMoS_2materials.

workwillbepursuedtobetterunderstandtheprocesskinetics.

Raman spectroscopy and mapping were carried out toprobethestructuralqualityofthecrystallizedMoS_2thinfilms. Figure 5(a) shows an optical image of a 5 × 5 crys-tallineMoS_2matrixpreparedby91 Wlaserpowerand30laserpulsesusingtheSLLCprocess.ThecorrespondingRamanmap ofthe matrix, figure 5(b), wasplotted forE^1_{2g} mode ofMoS_2at403cm^{-1}.Theuniformdistributionofthe Ramanintensityinthemapindicatedthespatialuniformityof thecrystallizedMoS_2dots.RepresentativeRamanspectraofthesamplefromtheamorphousandcrystallizedpartswereal soobtained,asshowninfigure5(c),indicatingintenseE^1_{2g}andA_{1g}RamanpeaksofMoS_2,similar totheresultsreported intheliterature[42].

CONCLUSION

In summary, we presented a novel SLLC approach by takingadvantage of significant contrasts in the optical properties ofamorphous and crystalline MoS_2 phases. We showed that theapproach could extend the crystallization process zone anddamagethresholdwellbeyondthenormallasercrystallizationprocesses.Alargenumberofdefects,imperfections,an dmidgapstatesintheamorphousfilmenhancedtheabsorption at below bandgap energies. We showed that a tunable nano-second (1064 nm) laser could be efficiently coupled into suchamorphous films to precisely heat the material, rearrange theatoms, and crystallize the film. Subsequently, due to appre-ciablechangesintheabsorptionpropertiesofMoS_2asit crystallized, the laser energy coupling efficiency dropped,leading to a self-limiting crystallization process with no fur-thereffectontheirradiated/crystallizedmaterials.Weshowed that the deliberate design of such laser 2D materialinteractionsviatheSLLCmethodenablesthematerialtohavea higher tolerance to process parameters in a much broaderprocessparameterwindow.Thismethodisespeciallyimportant for bringing a newalternativetothefutureflexible nanoelectronicsareawherehigh-performanceinorganicmaterials,suchas2Dcrystals,areofinterest.

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