Materials Science in Semiconductor Processing xx (xxxx) xxxx–xxxx

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Hyperdoping of Si by ion implantation and pulsed laser melting

Wenjie Yang[a,*], Jay Mathews[b], J.S. Williams[a]

[a] Department of Electronic Materials Engineering, Research School of Physics and Engineering, Australian National University, Canberra 2601, ACT, Australia

[b] Department of Physics, University of Dayton, 300 College Park, Dayton, OH 45469, USA

ARTICLE INFO

Keywords:
Ion implantation
Pulsed laser melting
Hyperdoped silicon
Intermediate band silicon
IR photodetectors
Laser annealing

ABSTRACT

Ion implantation followed by pulsed laser melting is an extensively-studied method for hyperdoping Si with impurity concentrations that exceed the equilibrium solubility limit by orders of magnitude. In the last decade, hyperdoped Si has attracted renewed interest for its potential as an intermediate band material. In this review, we first examine the important experimental results on both solid and liquid phase crystal regrowth from early laser annealing studies. The highly non-equilibrium regrowth kinetics following pulsed laser melting and its implications for dopant incorporation processes are discussed. We then review recent work in hyperdoped Si for enhanced sub-band gap photoresponse and give a brief discussion on photodetector device performance.

1. Introduction

Over the last 40 years, nanosecond and later femtosecond laser irradiation have emerged as an effective method for doping crystalline semiconductors with a range of impurities (initially introduced by ion implantation or some other method) to concentrations that greatly exceed their corresponding equilibrium solid solubility limit [1,2]. This unique class of materials has more recently been described as “hyperdoped” [3] to highlight their super-high non-equilibrium dopant concentrations whilst distinguishing them from conventional alloys and compounds.

During the last decade, hyperdoped Si has attracted special interest for its enhanced sub-band gap photoresponse, a property that can be exploited to fabricate Si-based optoelectronic devices in the near-infrared. This prospect is especially exciting given that Si, the dominating material in electronics with huge industrial exposure, is otherwise transparent in the near-infrared and thus a poor candidate for infrared photonics.

Despite the renewed interest, the history of forming non-equilibrium solid solutions by pulsed laser irradiation dates back to the 1970 s [4–6]. Laser annealing, as it was then called, had attracted wide attention for its promise in submicron scale electronics fabrication. While the initial interest for laser annealing was driven by its functionality in repairing implantation damage, specifically in recrystallizing amorphous layers, significant research effort has since gone into exploring novel materials and structures that emerged as a result of the high temperature gradient and concomitant rapid regrowth following energetic laser pulses. This pioneering work laid the foundation for present research on hyperdoped Si.

In this paper, we review some of the most important results from older laser annealing studies that are pertinent to the hyperdoping process, then focus on recent developments in utilizing hyperdoped Si for infrared optoelectronics, including device considerations. We conclude by outlining aspects of this hyperdoping approach that require further attention.

2. Early studies on removal of ion implantation damage

From the late 1960 s to 1970 s, ion implantation revolutionised the Si manufacturing industry as a technique that demonstrated a capacity for achieving highly controlled doping, both in terms of the dose and spatial distribution- attributes impossible to achieve by thermal diffusion. Early developments in ion implantation are reviewed by Fair [7] and are covered in more detail in [8]. However, the injection of highly energetic ions into a crystalline material disrupts the crystal lattice, causing damage and even amorphisation at sufficiently high implantation doses. As a result, a post-implantation annealing step is required for restoring crystallinity and for transporting the implanted dopants onto substitutional, electrically-active lattice sites.

The ‘annealing’ of ion implanted samples by laser irradiation was first demonstrated around the mid-1970s [5,6]. The initial motivation for studying laser annealing was twofold: i) to understand laser-solid interaction processes, particularly at very short (sub-millisecond) time scales, and ii) to pursue novel Si structures that are potentially important for integrated circuits, such as ultra-shallow junctions, small feature sizes and ultra-high doping [1]. Within the ensuing few years, a

* Corresponding author.
E-mail address: wenjie.yang@anu.edu.au (W. Yang).

http://dx.doi.org/10.1016/j.mssp.2016.11.005
Received 6 September 2016; Received in revised form 27 October 2016; Accepted 2 November 2016
Available online xxxx
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variety of different lasers and processing conditions were investigated, and it soon became well-established that both solid phase epitaxy (SPE) and liquid phase epitaxy (LPE) are possible outcomes of 'laser annealing'.

2.1. Solid phase epitaxy

Scanning continuous wave (cw) lasers (e.g. Ar ion lasers), with dwell times in the millisecond regime, cause semi-local heating of the near surface region of Si to temperatures approaching the melting point. As a direct consequence of thermally induced SPE regrowth, amorphous layers on a crystalline substrate can recrystallise upon cw laser irradiation [9,10]. In most instances, this growth mechanism can be reasonably explained by extrapolating (to higher temperatures and much shorter times) the regrowth conditions of furnace annealing, the most traditional and well-understood method for treating post-implantation damage in Si as patented by Shockley in 1957 [11].

During SPE, recrystallization occurs by the movement of an amorphous-crystalline interface towards the surface [12,13]. This process is rate limited by thermally-induced bond breaking and rearrangement at the amorphous-crystalline interface [14]. The epitaxial regrowth rate or interface velocity, v, is governed by an Arrhenius relationship:

$$v = v_0 \exp\left(\frac{-E_A}{kT}\right) \quad (1)$$

where E_A is the activation energy of the given material (typically 2.7 eV for silicon [15]), k is the Boltzmann constant, T is the temperature and v_o is a pre-exponential factor that depends on the crystallographic orientation of the substrate [16] and the impurity concentration at the interface [17]. Other factors such as strain [17,18] and hydrostatic pressure [19] have also been shown to affect the growth rate through v_O. More detailed considerations of the SPE process can be found in Refs. [15,20].

Compared with longer time, lower temperature furnace annealing, the regrown crystalline layer after cw laser irradiation was shown to exhibit several interesting and desirable properties. Most notably, it was demonstrated that, as a result of the localized heating and rapid heating/cooling rates, i) little diffusion occurs [21]; and ii) almost 100% electrical activity can be achieved even when the dopant (conventional p- and n-type) concentration exceeds the solid solubility limit [22]. For example, in As-implanted Si, the As profile after cw laser irradiation has been shown to be diffusion-free with a peak concentration roughly one order of magnitude higher than that achieved by thermal diffusion [9].

It is worth noting that the high dopant concentrations (above the solid solubility limit) achieved by cw lasers are also possible by other more conventional annealing (SPE) techniques. For example, Williams and Elliman [23] have shown that low temperature furnace anneals also allow higher than equilibrium concentrations (at least by one order of magnitude) of impurities to be incorporated under conditions in which negligible dopant diffusion occurs during recrystallization. Similar effects have also been observed in other isothermal (i.e. minimal bulk heating) annealing regimes based on flash lamps in the millisecond regime [24,25], and at longer time scales with halogen lamps [26], resistance heaters [27], and ion-beam-heating [28]. These more robust and cost-effective annealing methods, such as rapid thermal annealing (RTA) and flash lamp annealing (FLA), rather than laser annealing, have since dominated the Si integrated circuit industry for obtaining minimal dopant redistribution in the recrystallized Si [29–31]. Fig. 1 shows the Si regrowth rate as a function of temperature over the temperature/time regimes in which the different annealing techniques operate. The liquid phase regime associated with pulsed lasers of less than a few hundred nanoseconds will be treated in the next section.

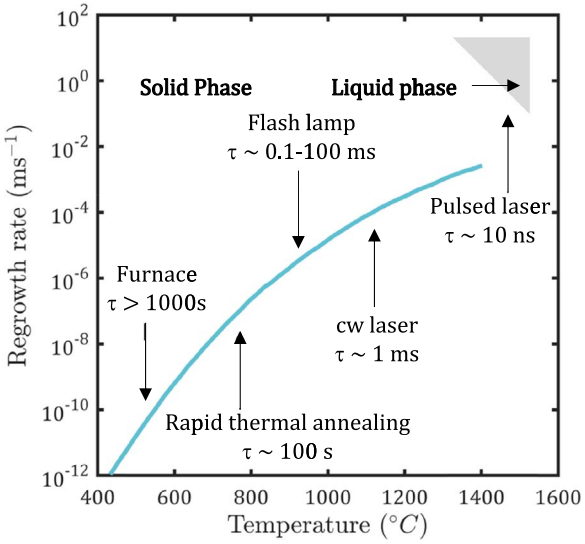

Fig. 1. Si regrowth rate in different solid and liquid phase epitaxy regimes. The grey area indicates the regime of liquid phase epitaxy where melting takes place. Figure adapted from Ref. [1].

2.2. Liquid phase epitaxy

In contrast to cw lasers, pulsed lasers (e.g. Ruby, Excimer and Nd:YAG) are capable of delivering intense beams (up to a few J/cm^2) in very short pulses (1–100 ns), enabling much faster regrowth from the single crystalline substrate. Under optimized conditions, pulsed lasers can achieve complete recrystallization of the implant-damaged layer without creating extended defects such as twinning and dislocations in the regrown material [32]. Time-resolved reflectivity measurements during the laser pulse [33], impurity redistribution profiles [34], surface segregation [35] and Nomarski contrast patterns on the surface following the laser treatment [36] provided strong experimental evidence that melting of the near-surface of Si (including the amorphous layer) occurs during the laser pulse. Following the pulse, liquid phase epitaxy (LPE) takes place as the molten layer rapidly resolidifies. For the remainder of this paper we shall refer to the use of pulsed lasers for melting and resolidification as *pulsed laser melting (PLM)*.

During PLM, the energy absorbed by the near-surface region is determined by the laser intensity, pulse duration, wavelength (which determines the absorption depth for a given material) and reflectivity from the surface [37]. If sufficient energy is delivered within a sufficiently short time frame, a thin layer melts with a thickness that is mainly dependent on the laser fluence (energy), as depicted in Fig. 2a, where the molten layer thickness is calculated from 1D heat flow calculations (adapted from ref. [1]). Since molten Si is largely metallic and absorbs more energy, melting propagates towards the bulk until the pulse ends. Heat is then quickly transferred away from the molten region due to the high temperature gradient between the molten layer and the surrounding material. This dissipated heat facilitates resolidification via LPE growth on the underlying crystalline template if the melt front has penetrated completely through an ion implanted amorphous layer. Insufficient penetration of the melt front and only partial melting of the amorphous layer results in a polycrystalline layer on complete solidification [38]. The movement of the solid/liquid interface (and the total melt duration) can be well monitored by time-resolved reflectivity measurements (TRR) with a probe laser, as shown in Fig. 2b, because molten Si is considerably more reflective than the solid. The melt duration can also be deduced from the reflectivity data, as shown in Fig. 2b).

The regrowth rate from a melt is thus primarily determined by the rate of latent heat extraction from the liquid/solid interface into the bulk substrate [39] as depicted in Eq. (2).

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